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ON THE COMBUSTION OF WEIGHED QUANTITIES OF HYDROGEN, AND THE ATOMIC WEIGHT OF OXYGEN.

BY E. H. KEISER.

The atomic weight of oxygen is the foundation upon which the entire system of atomic weights rests. It is unquestionably one of the most important constants in chemical science. At the present time the opinions of chemists differ as to its most probable value. While many accept 15.96 as the mean result of all the more trustworthy determinations, others are inclined to believe that the whole number 16 approaches nearer to the truth. Both numbers lie between the maximum and minimum values that have been obtained by the best methods heretofore employed in determining this constant. As all the other atomic weights, with few exceptions, depend upon that of oxygen, it follows that two values may be obtained for each element accordingly as one or the other of these numbers is made the basis of the calculation. As a result of this, all the atomic weights are uncertain to the extent of about one quarter per cent. of their values. It is very desirable for this reason, as well as for others of a more speculative nature—as, for example, the question of the validity of Prout's hypothesis—that the atomic weight of oxygen should be redetermined with the very greatest care.

In a preliminary paper[1] I called attention to a new method of determining this atomic weight, by means of which, it seemed to

[1] Ber. d. chem. Ges. **20**, 2323.

me, more accurate results could be obtained than by the older methods. Briefly stated, it consists in burning weighed quantities of hydrogen by passing the gas over heated copper oxide, and weighing the water formed. From the weight of water obtained by the combustion of a known weight of hydrogen, the atomic weight of oxygen may be readily calculated.

It is evident that the accuracy of the results obtained by this method must depend to a large extent upon the purity of the hydrogen that is used, and upon the correctness with which it is weighed. It is, however, extremely difficult to weigh accurately any considerable quantity of hydrogen in the gaseous state. If Regnault's method of compensated glass globes be used, it would require very large and heavy vessels to weigh comparatively small quantities of hydrogen, and in weighing such large globes errors may arise from many different sources. Lord Rayleigh[1] has recently pointed out a source of error in this method which appears to have been overlooked by all who had previously used it. He has shown that the volume of a glass globe is larger when it is full than when it is empty, and that the weight of the gas contained in it is not equal to the difference in weight of the full and empty globe.

In order to be able to weigh hydrogen accurately, I have taken advantage of the beautiful discovery made by Thomas Graham in the year 1866. Metallic palladium, as he has shown, has the power at ordinary temperatures of occluding many hundred times its own volume of hydrogen gas. The palladium hydrogen which is thus formed is stable at ordinary temperatures, and the metal retains the hydrogen even in a vacuum. If, however, the temperature be raised above 100°, then the gas will be expelled in a slow and regular current. Under atmospheric pressure nearly all of the hydrogen can be driven out at temperatures below 200°. By enclosing a quantity of metallic palladium in a glass vessel from which the air has been removed, and saturating it with pure hydrogen, a large volume of the gas may be condensed into a small space. If now the temperature be raised gradually, the gas will be driven out slowly and regularly. If the vessel be weighed before and after the heating, the loss in weight will equal the weight of hydrogen that has been expelled. It is possible, therefore, with an apparatus of small dimensions to weigh comparatively

[1] Chem. News **57**, 73.

large volumes of hydrogen. Preliminary experiments showed that 100 grams of palladium foil will readily absorb from .6 to .7 gram of hydrogen, and that with an apparatus having a volume of about 150 cc. and weighing 130 grams, it is possible to weigh, with great accuracy, an amount of hydrogen which in the gaseous state would occupy a volume of from 7 to 8 litres. A glass globe that could hold the same quantity of gas would be much heavier than the tube containing the palladium; and such a globe, owing to its much greater volume, could not be weighed with nearly the same degree of accuracy.

There is, however, another and no less important advantage gained in weighing hydrogen in the condition of palladium hydrogen. It is necessary that the hydrogen which is weighed and burnt for the purpose of determining the atomic weight of oxygen should be absolutely pure. The greatest difficulty connected with the preparation of pure hydrogen is to get rid of all traces of air. Other impurities may be avoided by starting with chemically pure materials for the preparation of the gas, and by using appropriate absorbing and drying reagents for purifying it. If air is present, the oxygen of the air may be removed by passing the gas over heated copper. Water will be formed, and this may be absorbed by means of phosphorus pentoxide. But there is no way of removing the nitrogen. Palladium, however, has not the power of absorbing nitrogen. If the hydrogen used for saturating the palladium contains nitrogen, the hydrogen will be occluded, the nitrogen will remain unacted upon; and, after the palladium has been saturated, the nitrogen may be removed from the palladium tube by means of an air pump.

Thomas Graham,[1] who first studied the behavior of palladium toward gases, found that hydrogen was the only constituent of illuminating gas that possessed the power of penetrating palladium foil. Wöhler[2] has shown that palladium cannot absorb ethylene, and that at high temperatures it decomposes hydrocarbons into carbon and hydrogen. Wilm[3] has also observed that at high temperatures palladium can decompose hydrocarbons, and he has shown that the hydrogen is absorbed by the metal, while the carbon is left on its surface in an extremely finely divided condition. Hempel[4] has found that from a gas mixture containing hydrogen,

[1] Ann. Chem. (Liebig) Supp. Band **5**, 61.
[2] Ann. Chem. (Liebig) **184**, 129.
[3] Ber. d. chem. Ges. **14**, 874.
[4] Ber. d. chem. Ges. **12**, 636.

marsh gas, and nitrogen, the hydrogen may be completely absorbed and separated from the other constituents by means of metallic palladium.

Preliminary Experiments.

While it thus appears from a study of the literature of palladium that this metal has not the power of absorbing nitrogen or marsh gas, ethylene, and other hydrocarbons, it, nevertheless, seemed necessary to determine by careful preliminary experiments whether, under the conditions under which the palladium was to be used for occluding hydrogen, it might not be able to take up minute traces of nitrogen or oxygen. For this purpose several pieces of palladium foil, weighing together 140 grams, after being carefully cleaned and rolled into the shape of a cylinder, were placed in a wide glass tube which was closed at one end. The open end was drawn down to a small diameter and fused to a three-way glass stop-cock. The tube was exhausted with a Geissler air pump and the metal heated to a temperature of about 400° in the vacuum. The glass tube was protected from the flame by a wrought iron trough containing a layer of magnesia. After the metal had been heated for some minutes in the vacuum, the lamp was removed. Pure dry nitrogen gas was then admitted by means of the three-way stop-cock, and the metal was allowed to cool down slowly and to remain for several hours in an atmosphere of nitrogen. The tube was thereupon exhausted with the pump and, after a vacuum had been obtained, it was again heated. Not the minutest trace of gas was given off. If only a small fraction of a cubic centimeter of nitrogen had been driven out of the palladium it would have been detected because the pump was kept in constant operation. The experiment was repeated several times, but the result was always the same. In one experiment the palladium tube was exhausted and weighed. It was then heated in the vacuum and treated with nitrogen as above described. After being again exhausted the weight was found to be the same as before. It appears, therefore, that under these conditions palladium has not the power of absorbing nitrogen; but these are the conditions that were found to be the most favorable for the occlusion of hydrogen. After the metal had been heated in a vacuum it was allowed to cool in an atmosphere of hydrogen. The gas was absorbed in large quantities. When perfectly cold the tube was exhausted and

weighed. It was found to be nearly a gram heavier than it was before the hydrogen had been occluded. The hydrogen was held so firmly by the palladium that when the tube was exhausted with the air pump the palladium hydrogen showed but a very slight tension. On warming it, however, the gas was given off in large quantities. Other experiments made with oxygen showed that this gas also, under the conditions described above, is not absorbed by palladium.

Experiments were now made for the purpose of determining what the effect would be of treating palladium with hydrogen containing a small percentage of air. The metal was heated in a vacuum and then allowed to cool in an atmosphere of hydrogen containing air. The hydrogen was rapidly absorbed, but at the same time a minute quantity of moisture was deposited on the interior surface of the tube. When no more gas was absorbed the palladium tube was connected with a weighed phosphorus pentoxide U tube and heated. As the gas escaped from the palladium tube the film of moisture gradually disappeared. The U tube was weighed again after the hydrogen in it had been displaced by air. It was found to have increased in weight, thus showing that when palladium is treated with hydrogen containing air the oxygen is converted into water. The idea suggested itself that perhaps hydrogen dioxide might also be formed, and that the palladium hydrogen in the presence of nitrogen might cause the formation of ammonia. The palladium was therefore treated again with hydrogen containing air, and after the metal had been saturated the palladium tube was connected with a Geissler potash bulb containing Nessler's solution. The gas was thereupon driven out of the palladium tube by heating, and although more than six litres of hydrogen were passed through the Nessler's solution, not the faintest reaction for ammonia was obtained. The experiment was repeated, but in this case, instead of using Nessler's reagent, the gas from the palladium tube was led through a solution of potassium iodide and starch paste to which a small quantity of ferrous sulphate had been added. No reaction for hydrogen dioxide was obtained. Another experiment was made for the purpose of determining whether palladium itself is not volatilised when palladium hydrogen is decomposed. A quantity of palladium foil was carefully weighed and then saturated with hydrogen. The hydrogen was then completely removed by heating in the presence of air. On weighing the foil again its weight was found to be unchanged.

The conclusions drawn from the results of these preliminary experiments are as follows: Palladium at temperatures below 400° cannot occlude oxygen or nitrogen. If palladium be treated with hydrogen containing a trace of nitrogen, the hydrogen will be occluded, but the nitrogen will remain unabsorbed, and it may be removed from the vessel containing the palladium hydrogen by means of an air pump. If the tube containing the palladium hydrogen be heated pure hydrogen will be expelled, and the weight of the gas thus driven out may be determined from the loss in weight of the palladium tube. If palladium be treated with hydrogen containing traces of air, the hydrogen will be occluded, the nitrogen will remain unabsorbed, but the oxygen will be converted into water. By means of an air pump the nitrogen and a portion of the water may be removed from the tube containing the palladium. On heating the tube the hydrogen which is driven out will carry with it traces of moisture. The weight of the hydrogen and moisture thus expelled may be determined from the loss in weight of the palladium tube, and the amount of moisture present in the hydrogen may be determined by passing the gas through a weighed phosphorus pentoxide U tube. Lastly, palladium itself is not volatilised when palladium hydrogen is decomposed.

Apparatus for Preparing and Weighing the Hydrogen.

The construction of the palladium tube that was used for weighing the hydrogen in the atomic weight determinations is shown in Fig. 1. The expanded portion *a* contained 140 grams of palladium foil that had previously been thoroughly cleaned, and which, before being placed in the tube, had been heated to a bright red heat in a vacuum. The three-way glass stop-cock *b* was fused to *a*, and its construction will be readily understood from the cross-section drawing *b'*. The end *c* was ground to fit accurately into the phosphorus pentoxide tube *d*, shown in Fig. 3. The diameter of *a* was 3 cm. and its length 14 cm. The total length of the tube including the stop-cock was 26 cm.; its weight, including that of the palladium, was 204.5 grams. The first six determinations were made with a somewhat smaller tube which contained only 100 grams of palladium and weighed 160 grams.

The hydrogen that was used for saturating the metal was prepared by the action of pure dilute sulphuric acid upon chemically

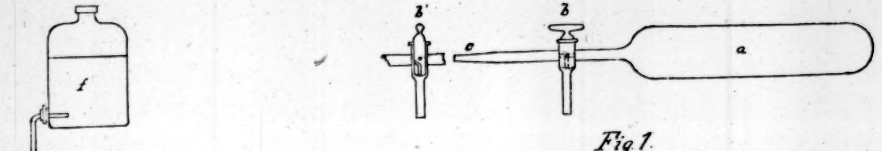


Fig 1.

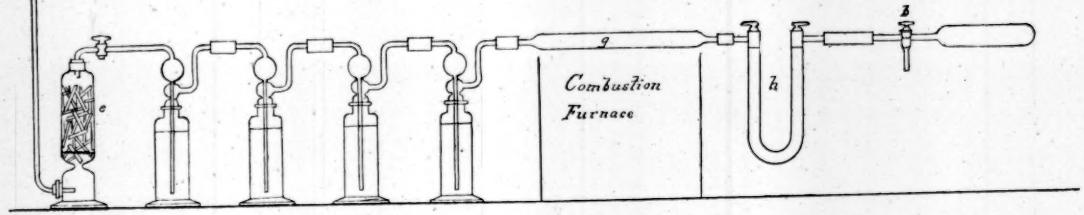


Fig. 2

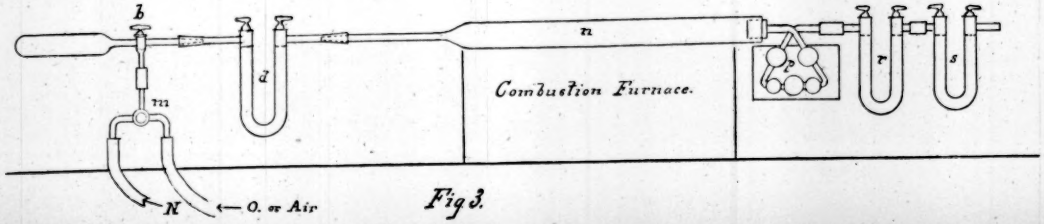


Fig 3.

pure zinc, free from arsenic. The apparatus for generating and purifying the gas is shown in Fig. 2. The zinc was placed in *e*, and it was acted upon by the dilute sulphuric acid contained in *f*. The vessel *f* was supported by a shelf, and was connected with *e* by means of glass tubing as shown in the figure. After leaving the generating apparatus the hydrogen passed through four wash-bottles. The first one contained a solution of lead hydroxide in concentrated caustic potash; the second one, a concentrated solution of potassium permanganate acidulated with dilute sulphuric acid; the third one, an alkaline solution of potassium permanganate; and the fourth one, pure concentrated sulphuric acid. To the fourth wash-bottle was connected the combustion tube *g*, which contained metallic copper. The copper was obtained by the reduction of the chemically pure oxide in a current of hydrogen. A small gas furnace supported the combustion tube, and while the gas was being generated the tube was kept at a bright red heat. After having passed over the heated copper the gas was conducted through the U tube *h*, which was filled with phosphorus pentoxide. The joints of the apparatus were made of thick-walled rubber tubing; they were all wired securely and coated with varnish.

The method of charging the palladium with hydrogen was conducted as follows: The palladium tube, resting upon a trough of sheet iron and protected from contact with the iron by a layer of magnesia, was connected with a Geissler air pump and exhausted. After the palladium had been heated to a temperature of about 250° for fifteen minutes in the vacuum, the stop-cock *b* was closed, and, while the tube was still warm, the end *c* was connected with the U tube *h* as shown in Fig. 2. Meanwhile all the air in the hydrogen generating apparatus and the wash-bottles had been expelled, as the evolution of gas was begun more than one half hour before the palladium tube was attached. For several minutes more the hydrogen was allowed to escape from the downward branch of the stop-cock, to which a straight glass tube dipping in mercury was attached, to ensure that all the air had been displaced in the tube connecting the palladium vessel with the U tube *h*. The stop-cock was then turned carefully so as to allow a slow stream of hydrogen to enter the warm palladium tube. Under these circumstances the metal absorbs the hydrogen so rapidly that it is necessary to open the stop-cock very cautiously, otherwise the gas will pass too rapidly through the wash-bottles.

While the hydrogen is being absorbed the metal cools down very slowly, because considerable heat is evolved in the formation of palladium hydrogen. When the absorption of gas had become very slow—and from 2 to 2½ hours sufficed for saturating 140 grams of palladium—the stop-cock was closed and, after being again attached to the Geissler pump, the tube was exhausted. By this means nitrogen, if it should have been present in the hydrogen used for saturating the palladium, was removed. Palladium hydrogen gives off hydrogen very slowly in a vacuum, so that, if the pump be kept in operation for some time, all traces of nitrogen in the palladium tube and in the pump itself may be completely carried out by means of this slow evolution of gas. After the removal of the nitrogen the tube was closed and disconnected from the pump. It was then thoroughly cleaned and placed in the balance room.

A short beam analytical balance, made by Becker Brothers, New York, was used for all the weighings. It could carry safely 225 grams in each scale pan, and was adjusted so that a load of one milligram caused a deflection of 12 divisions of the ivory scale. All weighings were made by the method of vibrations. In weighing the palladium tube and the tubes used for condensing and absorbing the water, each tube was compensated by a similar one, of the same external volume, constructed of the same material, and having nearly the same weight. The weights were also made by Becker Brothers; the smaller ones were of platinum, the larger ones of brass. One of the 10 gram weights was selected as the standard, and the relative values of all the others were determined by the well known method of adjustment. All atomic weight determinations were made on days when the weather was clear and dry; and, as a combustion including the weighings could be made in four hours, the barometer, temperature of balance-room, and the humidity of the air remained practically constant during each determination.

Method of Burning the Hydrogen.

The arrangement of the apparatus that was used for burning the hydrogen is shown in Fig. 3. The palladium tube was connected by means of a ground-glass joint with the weighed phosphorus pentoxide tube *d*. The latter tube served to determine the amount of moisture in the hydrogen that was expelled from the palladium tube. The tube *d* was connected by means of

another ground-glass joint with the combustion tube *n*, which contained copper oxide. For the purpose of obtaining pure copper oxide, the chemically pure granular oxide of commerce was reduced in a current of pure hydrogen, and the metallic copper thus obtained was heated to a bright red heat in a vacuum. All volatile matter having been removed in this way, the copper was oxidised with pure oxygen. In each determination the reduced copper was again oxidised to copper oxide, so that the condition of the combustion tube was the same at the beginning and end of the combustion. The copper oxide that was used in the determinations recorded below had been repeatedly reduced and oxidised in preliminary determinations. The combustion tube was 90 cm. in length and had an internal diameter of 15 mm. It was filled to within 10 cm. of the open end, and it contained so much copper oxide that there was never more than one half of it reduced in any determination. The object of this large excess was to insure the complete combustion of the hydrogen. The water formed by the combustion of the hydrogen was condensed in the bulb apparatus *p* and the U tube *r*. When not connected with the combustion tube, *p* was closed by means of ground-glass plugs. A tightly fitting rubber stopper was used to connect the bulb apparatus with the combustion tube. During the combustion the bulbs were kept cool by being surrounded with cold water placed in a glass dish. The U tubes *r* and *s* contained phosphorus pentoxide, and *s* served to protect *r* in case air should be drawn backward into the combustion tube. To the downward branch of the stop-cock of the palladium tube was attached the three-way glass stop-cock *m*, by means of which either oxygen or nitrogen could be passed through the apparatus. The oxygen before entering was conducted through concentrated sulphuric acid, concentrated caustic potash, and over phosphorus pentoxide. The nitrogen was purified by passing through concentrated sulphuric acid, concentrated caustic potash, over red-hot copper to remove the oxygen, and then over phosphorus pentoxide.

The combustion of the hydrogen was conducted in the following manner: In the first place, the copper oxide was heated to a bright red heat in a current of dry air so as to remove hygroscopic moisture. The U tube *d*, the palladium tube, and the tubes *p* and *r*, after having been carefully weighed, were connected as shown in Fig. 3. The tube *s* and the stop-cock *m* were then attached, and a stream of nitrogen was allowed to pass through

the apparatus for from 20 to 30 minutes to expel the air, thus avoiding the possibility of an explosion when the hydrogen was admitted. The palladium tube was thereupon warmed gently, and, after its temperature had risen to a little above 100°, the stop-cock *b* was turned slowly so as to cut off the current of nitrogen and to allow a slow stream of hydrogen to pass through *d* into the copper oxide tube. In warming the palladium tube the flame never came in contact with the glass. The tube was always supported by an iron trough, and the glass was protected from contact with the iron by a layer of magnesia. The rate at which the gas was expelled and burnt could be easily regulated by raising or lowering the temperature of the palladium tube. After the greater quantity of hydrogen had been burnt and the current of gas had become very slow, the stop-cock *b* was turned to its original position, thus closing the palladium vessel and readmitting the stream of nitrogen. The palladium tube was then allowed to cool; in so doing the metal reabsorbs the gaseous hydrogen that is present in the tube, and at the end of the operation the pressure in the interior of the tube is the same as at the beginning. After the nitrogen had carried all of the hydrogen into the combustion tube, oxygen was admitted through *m*, and the reduced copper was converted into copper oxide. The oxygen was then displaced by a stream of dry air, and the copper oxide was allowed to cool.[1] The tubes were then disconnected and, after being cleaned, were taken to the balance room. They were allowed to stand a sufficient length of time to acquire the temperature of the room, and were then weighed.

The weight of water formed was determined from the increase in weight of *p* and *r*. To the weight of liquid water in *p* was added the weight of air which it displaced, thus its weight in vacuo was

[1] For the purpose of determining whether traces of hydrogen could escape combustion by this method, the following experiment was made: About one half of the copper oxide in the combustion tube was reduced with hydrogen, then a current of carbon dioxide was allowed to enter at *m* so as to carry all of the hydrogen into the combustion tube. The gases after passing over the copper oxide were conducted through caustic potash, then over phosphorus pentoxide, and again over copper oxide contained in a second combustion tube. To this second combustion tube was attached a weighed phosphorus pentoxide tube. If any hydrogen should have escaped combustion in the first combustion tube, where it was diluted with a large excess of carbon dioxide, it must have accumulated in the caustic potash bulbs. Subsequently when air was drawn through the apparatus, the hydrogen would have been carried into the second combustion tube in much more concentrated condition than it left the first one. In this tube it would have been burnt, and the phosphorus pentoxide tube would have increased in weight. Although the experiment was tried several times, the weight of the latter tube always remained constant.

obtained. The weight of the tube *d* remained the same as at the beginning of the combustion, provided the hydrogen that had been used for saturating the palladium was free from oxygen. In this case the loss in weight of the palladium tube gave the weight of hydrogen that had been burnt. If, however, a small quantity of oxygen was present in the hydrogen used for charging the palladium, then the gas that was expelled from the tube contained a trace of moisture, and, in this case, the increase in weight of *d* had to be deducted from the apparent weight of hydrogen. In all carefully conducted atomic weight determinations the increase in weight of *d* was never found to be more than a fraction of a milligram.

Atomic Weight of Oxygen.

The following results have been obtained by this method:

No. of Experiment.	Wt. of H burnt.	Wt. of Water Obtained.	Atomic Wt. of Oxygen.
1	.34145 grams.	3.06338 grams.	15.943
2	.68394	6.14000	15.955
3	.65529	5.88200	15.952
4	.65295	5.86206	15.954
5	.66664	5.98116	15.944
6	.66647	5.98341	15.955
7	.57967	5.20493	15.958
8	.66254	5.94758	15.952
9	.87770	7.86775	15.950
10	.77215	6.93036	15.951
Total	6.55880	58.86263	[15.9492]

From these numbers the ratio of hydrogen to oxygen is found to be: H : O :: 6.55880 : 52.30383, or H : O :: 1 : 7.9746, and the atomic weight of oxygen = 7.9746 × 2 = 15.9492. Maximum value 15.958; minimum value 15.943. The result obtained from these determinations appears, in the author's mind, to furnish very strong evidence in favor of the view that the relative atomic weight of oxygen cannot be greater than 15.96, and that its true value is probably a little less than this number.

Several months after the appearance of my preliminary paper, and while this investigation was still in progress, Prof. J. P. Cooke and Mr. T. W. Richards published the results of a redetermination of the atomic weight of oxygen by the same general method which

I had proposed. They also have determined the quantities of water formed by the combustion of weighed amounts of hydrogen. But our work differs very much in the methods employed for weighing the hydrogen. Messrs. Cooke and Richards have weighed it in the gaseous state, and have used Regnault's method of weighing gases by means of compensated glass globes. Aside from the difficulties of weighing accurately such large glass globes, owing to air currents, changes of atmospheric conditions, etc., and the fact that a comparatively heavy vessel must be used for weighing but a small quantity of hydrogen; this method is open to the objection that all impurities that may be present in the gas, such as traces of nitrogen or air, are weighed as hydrogen. Errors caused by impurities in the hydrogen tend to diminish the atomic weight of oxygen. On the other hand, Lord Rayleigh has pointed out another source of error which tends to increase the atomic weight. As mentioned above, the volume of a glass globe is not the same when it is full and when it is empty, and the difference between the full and empty weighings is less than the true weight of hydrogen.

The method which I have employed for obtaining weighed quantities of hydrogen seems to me to be free from these sources of error. By using palladium, a considerably larger quantity of hydrogen may be obtained from a very much smaller and lighter apparatus, consequently the gas can be weighed with greater accuracy. Impurities such as nitrogen and oxygen are eliminated, and as the pressure in the interior of the palladium tube is the same at the beginning and end of the determination, and as the vessel is of small dimensions, there can be no change of volume of the tube. Nevertheless the value for the atomic weight of oxygen obtained by Messrs. Cooke and Richards agrees very closely with that obtained by this method. Value obtained by Cooke and Richards $= 15.953$.[1] Value obtained by the palladium method $= 15.949$.

That our results do not differ more is probably due to the fact that the errors in the method used by Messrs. Cooke and Richards are in opposite directions and tend to neutralise each other.

Bryn Mawr, Pa., *April*, 1888.

[1] Professor Cooke has recently determined the value of the error caused by the change in volume of the glass globe. He finds the corrected atomic weight of oxygen to be 15.869. This result, it seems to me, is undoubtedly too low. In my preliminary experiments (Ber. d. chem. Ges. **20**, 2323), before the precaution was taken to remove traces of nitrogen by exhausting the tube containing the palladium hydrogen, nearly the same figure was obtained, viz. 15.872.

Contributions from the Chemical Laboratory of Wesleyan University.

VIII.—ON SOURCES OF ERROR IN DETERMINATIONS OF NITROGEN BY SODA-LIME AND MEANS FOR AVOIDING THEM.

By W. O. Atwater.

[Concluded from p. 209.]

Loss by Dissociation and Oxidation of Ammonia.

It is frequently urged that in the determination of nitrogen with soda-lime, ammonia may be dissociated at the temperature at which the combustions are conducted, and that in aspirating air through the tube at the end of the operation some of the ammonia may be burned. The following experiments were made in the hope of getting light upon the conditions under which such loss may thus occur in determinations as ordinarily made.

For this purpose means were taken to test the effects of (1) unusually long exposure of the ammonia to heat, (2) very high heat, and (3) exclusion of air. Ammonia was furnished by ammonium sulphate in which the ammonia had been determined by distillation by the method described by Gooch,[1] two determinations giving respectively 21.11 and 21.14, and averaging 21.13 per cent. of nitrogen. About 0.3 gram mixed with from 0.5 to 1.0 gram of oxalic acid previously proven to be free from nitrogen were employed in each of the determinations detailed beyond. The soda-lime, made from 1 part of caustic soda and 2½ of lime, and the method of charging the tube, were as previously described.[2] The method, which is that usually followed in this laboratory, involves filling the tube quite full of soda-lime, so as to avoid large open spaces which become filled with gases and allow long sojourn of ammonia in the tube. Where the long tubes were used, the length of the anterior layer of coarse fragments of soda-lime was increased with the length of the tube, the length of mixture of soda-lime and nitrogenous substance and the charging otherwise remaining the same as in the tubes of ordinary length. The time of combustion, about 30 to 35 minutes, was naturally a little less than would usually be the case with animal tissues. The flames

[1] This Journal **1**, 450. [2] Ibid. **9**, 319.

were turned off at the close of the combustion before the aspiration with air to wash out the ammonia. In No. 10 (see Table II) the air was expelled before the combustion, and the ammonia washed out at the end by carbonic acid. In Nos. 11 to 19 the expulsion of air and cleaning out of ammonia were effected by a current of hydrogen which was delivered by a generator so arranged as to permit easy regulation of the flow. The hydrogen was passed over heated copper foil, to remove the oxygen, before entering the combustion tube.

Five series of trials were made. Previous experience had persuaded us that when (1) the tubes are of moderate length and compactly filled with soda-lime, (2) only a moderately high heat is used, (3) the combustion does not proceed too slowly, and (4) the flames are turned off and the tube allowed to cool slightly before aspirating with air, there is no considerable loss of nitrogen by either dissociation or oxidation. In the first series, in which the operation was conducted in the usual way, a confirmation of this impression was sought. In the second series the effect of increasing the length of the tube and with it the time of sojourn of the ammonia gas in the tubes, without increasing the heat, was observed. In the third series the effect of high heat was tested by using long tubes as in the second series, and making the heat much greater. In the fourth series it was sought to learn whether the loss of nitrogen observed in the third series was due to dissociation or to oxidation, or to both. The trials of the fifth series had a similar object. The results are given in detail in Table II, which includes all the determinations made, and are recapitulated in Table III.

The figures of the first series indicate that with tubes of our ordinary length, 40 cm. or a little less, compactly filled (about 16 cm. with mixture of fine soda-lime and substance, 4 cm. with "rinsings" of fine soda-lime, and 12 cm. with an anterior layer of coarse soda-lime), at a heat sufficient to make the tube dull red, designated here as "medium," and with aspiration by air after the tubes had begun to cool, there was no loss of nitrogen.

In the second series the tubes were long enough to make the anterior layer of coarse soda-lime about 35–40 cm.; the charging otherwise was the same as in the first series. The percentage of nitrogen obtained was the same. Lengthening the tube had no effect upon the result. At moderate heat there was no loss by dis-

TABLE II.

Determinations of Nitrogen in Ammonium Sulphate under Different Conditions.

By distillation, 21.11 and 21.14, average 21.13 per cent.

By Soda-lime.

Series.	No.	Length of Tube, cm.	Heat.	Aspirated with.	Nitrogen found, Per cent.		
					Separate Determinations.	Average.	Range of Variation.
1st	1	42	Medium.	Air.	21.12		
	2	42	"	"	21.10		
	3	35	"	"	21.13	21.12	.03
2d	4	75	"	"	21.11		
	5	75	"	"	21.12		
	6	75	"	"	21.11		
	7	75	"	"	21.12	21.12	.01
3d	8	75	High.	"	20.80		
	9	75	"	"	20.86	20.83	.06
4th	10	75	"	Carbonic acid.	20.91		
	11	75	"	Hydrogen and pump.	20.70		
	12	75	"	" "	20.81		
	13	75	"	" "	20.84		
	14	75	"	" "	20.90	20.83	.21
5th	15	75	Medium.	" "	21.10		
	16	75	"	" "	21.10		
	17	75	"	" "	21.12		
	18	75	"	" "	21.11		
	19	75	"	" "	21.13	21.11	.03

TABLE III.

Recapitulation of Determinations of Nitrogen in Ammonium Sulphate under Different Conditions.

Series.	Length of Tube and Anterior Layer of Soda-lime.	Heat of Combustion.	Aspirated with.	Nitrogen found.		Loss of Nitrogen in per cent. of total Nitrogen.	
				Average.	Range of Variation.	Maxim'm.	Aver'ge.
				Per cent.	Per cent.	Per cent.	Per ct.
1st.	Usual.[1]	Medium.	Air.	21.12	0.03	...	...
2d.	Very long.[2]	Medium.	Air.	21.12	0.01	...	...
3d.	Very long.[2]	High.	Air.[3]	20.83	0.06	1.5	1.4
4th.	Very long.[2]	High.	Hydrogen.	20.83	0.21	2.0	1.4
5th.	Very long.[2]	Medium.	Hydrogen.	21.11	0.03	...	...

[1] Tube about 40 cm., anterior layer of soda-lime about 12 cm.

[2] Tube 75 cm., anterior layer about 35-40 cm.

[3] In one case with carbonic acid.

sociation with closely packed tubes even when the latter were very long and the exposure of the ammonia to the heat was increased.

In the third series the conditions were the same as in the second except that the temperature was made as high as the tubes, of the most difficultly fusible Bohemian glass we could obtain, would endure without bursting. The standard acid employed was rather concentrated, so that but a small quantity was needed in the nitrogen bulb and the internal pressure was thus reduced to a minimum. It was thus possible to heat the tubes to bright redness without their bulging. Instead of 21.12, only 20.83 per cent. of nitrogen was obtained. This falls short of the actual amount by 0.29 per cent. of the weight of the sulphate of ammonia, or 1.4 per cent. of the total nitrogen. The indication of loss by either decomposition or oxidation of ammonia was very apparent.

In the fourth series the conditions were the same as in the third except that air was excluded, the object being to find, if practicable, how much of the loss in the previous series was due to the burning of ammonia by the oxygen of the air, and how much to dissociation. In No. 10 the length of the tube was actually 80 cm. instead of 75 cm., as in the other cases. The extra 5 cm. of the posterior end were filled with bicarbonate of soda, which was heated at the beginning of the experiment to expel the air present in the tube, and again at the end to drive out the residual ammonia. In Nos. 11 to 14, as in all of the next series, in which hydrogen was used for the same purpose, the tubes were about 80 cm. long or a little longer, the extra 5 cm. at the posterior end being filled with asbestos. The hydrogen, which had been dried by sulphuric acid, was passed through the combustion tube for three quarters of an hour, and the tube was then exhausted by a mercury pump, after which hydrogen was again passed through for half an hour. Assuming that the air had thus been very nearly all removed, the combustion was conducted at the very high heat, as in the third series. When it was done, hydrogen was again passed through to wash out the residual gases, precautions being taken to admit no air. The amount of nitrogen obtained averaged the same as in the third series, 20.83 per cent. The exclusion of air made, then, no difference in the result. This indicated that the loss was due not to oxidation, but to dissociation of ammonia.

It is observable, furthermore, that the individual results in the third and fourth series vary considerably, the range in the fourth

series being .21, while in the first and second series it was only .03 per cent. While the agreement of duplicates is a very uncertain evidence of the correctness of an analysis, a wide disagreement may be regarded as a tolerably sure indication of error.

In the fifth series the conditions were the same as in the fourth, except that the combustion was made at "medium" heat. The results, which average 21.11 per cent., are practically identical with each other and with those of the first and second series. The difference in conditions between this and the fourth series, like that between the second and third, is simply one of heat, and that difference in each case evidently makes the whole of the difference in result.

To resume:—In every case in which the medium heat was employed, whether with long or with short tubes, whether with or without air, the full amount of nitrogen was obtained. In every case with the high heat there was a loss from 1 to 2 per cent. of the total nitrogen in the substance. Neither the length of the tubes nor the presence or absence of air made any difference in either the amount of nitrogen obtained or the uniformity of the results, but the high heat materially reduced the amount of nitrogen and made wide variations in results of duplicate determinations.

That more definite statements as to temperature at which the dissociation takes place are to be desired, goes without saying. Ramsay and Young,[1] in a series of very interesting experiments on the temperature of dissociation of ammonia, find that the point at which it commences varies greatly with the nature of the surrounding medium. In a porcelain tube filled with broken pieces of porcelain, in an iron tube filled with porcelain, and in a glass tube filled with ignited "porous" asbestos cardboard to expose the gas to a large surface, the decomposition commenced at about 500° or below. At 500°–520°, however, it was very small, but increased greatly at higher temperatures. In contact with a glass surface the temperature at which decomposition begins was much higher. The nature of the surface heated has a very great influence on the amount of ammonia decomposed. In a plain dry iron tube the decomposition was apparently complete at 780°, but if water was present, only 95 per cent. was decomposed. At 760°, in a glass tube containing iron wire, 74.3—76 per cent. of the ammonia was decomposed; but when copper was substituted (the other condi-

[1] J. Chem. Soc. 1884, Proc. p. 88.

tions remaining essentially unaltered), only 2.0 per cent. was decomposed. The authors find that "the amount of decomposition depends partly upon the rate of passage of the gas, or in other words, on the time of exposure to heat," and that "the extent of surface also influences the amount of decomposition."

From these results, as well as from consideration of what is known of dissociation in general, it is evidently impossible to predicate anything definite regarding the amount of decomposition that would take place at a given temperature in a glass tube containing soda-lime and such a complex mixture of gases as occur in an ordinary combustion. I regret the lack of facilities which prevented determinations of the temperature at which the combustions in these experiments were made. But so far as one can judge from observation, I should say that what I have here designated as "medium heat" or "usual heat," namely, that in which the combustion tube is dull red and the soda-lime yellowish, is about that at which combustions are very commonly made in the laboratories where I am acquainted.

Prehn and Hornberger[1] have reported observations which imply large losses of nitrogen by oxidation in soda-lime combustions. When sugar was burned in the tube to expel the air before the combustion and to sweep out the ammonia afterwards, considerably more ammonia was obtained than where this precaution was omitted, and the apparent oxidation by the air present in the tube at the beginning was greater than that from the air used in the aspiration at the end. But the experiments were made with ammonium salts, and where no sugar was used there was apparently no gas to drive out the air and prevent its oxygen from acting on the ammonia. In ordinary combustion of nitrogenous materials large quantities of gases are produced, and in the experiments I have just described oxalic acid was used, which naturally drove out the air.

On the other hand, numerous analysts[2] find that with proper precautions there is no loss from oxidation. In our work we have taken pains to have the tubes well filled with soda-lime and substance so as to leave only very little open space for air, and to heat the anterior layer of soda-lime before applying the heat to the mixture of soda-lime and substance, thus expelling a large part of

[1] Landw. Vs. St. **24**, 21.

[2] e. g. vid. Gruber, Zeitschr. Biol. **16**, 374, and Johnson and Jenkins, this Journal **1**, 77.

the air in advance, and have been careful not to aspirate with air until after putting out the flames so that the contents of the tube have become somewhat cooled before the air has been admitted. In how far omission of these precautions may explain the apparent oxidation elsewhere observed, I of course cannot say. Naturally there would be the less danger of loss the more the air is removed by diluting gases before heating. But considerable experience has left me with the very strong impression that with the precautions I have suggested there need be very little fear of oxidation. This must be especially true where, as in ordinary combustions, large amounts of hydrocarbons are present to combine with the oxygen.

Makris has shown that oxidation may take place, but his experiments were made under conditions especially arranged to insure admixture of air with ammonia at a high temperature.[1]

Prehn and Hornberger have also experimented upon the effect of different degrees of heat on the ammonia in determinations with ammonium salts and potassium ferrocyanide. They find, at what they call ordinary heat or dull redness, no considerable indications of dissociation, but on heating to bright redness they found with tubes 35–40 cm. and the anterior layer of soda-lime 15 cm. long, considerable, and with tubes 55–65 cm. and the anterior layer 30–40 cm. still more indication of the dissociation of ammonia. Their results thus agree with those above given, except that they get more dissociation with the high heat in the long than in the short tubes. This they very reasonably explain by the fact that the ammonia in the long tubes had more time to dissociate, from which I infer that the gases were caused to pass more slowly than was the case in our work.

Makris also tested the dissociation of ammonia by passing a slow current of gas through a tube 70 cm. long filled with pieces of soda-lime and heated to bright redness. Analysis of the gases coming from the tube showed a very considerable amount of dissociation. But, as Gruber has observed, the case here was different from that in an ordinary combustion, in that a large amount of ammonia was exposed for a long time to a high heat and without any considerable amount of diluting gas, whereas in ordinary combustion there is less free space in the tube and that largely filled with other gases, so that the ammonia is rapidly swept away, and furthermore the

[1] Ann. Chem. (Liebig) **184**, 376.

diluting gases are largely hydrocarbons which would naturally furnish nascent hydrogen to regenerate dissociated ammonia.

My results above detailed accord very exactly with those of Gruber and of Johnson and Jenkins above cited, who found no indications of loss by dissociation. But it is evident that both the complete transformation of nitrogen into ammonia, and the loss of ammonia, depend largely upon the manipulation. Thus Kissling gets very good results with an anterior layer 35 cm. long, and evident loss of nitrogen when the anterior layer is only from 7 to 10 cm. long, the combustion being carried on slowly.[1]

The experiments described by Mr. Ball and myself in a previous article[2] bear upon the questions of dissociation of ammonia and of incomplete ammonification of nitrogen of distillation products. They were made with casein, the conditions being varied so as to allow in some cases very little, and in others considerable opportunity for the ammonia formed to be dissociated. The results, given in detail in the article referred to, are more concisely set forth in Table IV, herewith.

TABLE IV.

Effects of long heating and of open space in tube upon amounts of nitrogen obtained as ammonia from casein containing 12.43 *per cent. of nitrogen.*

Conditions of Experiments.	Nitrogen Lost.					
	In per cent. of Weight of Casein.			In per cent. of Total Nitrogen.		
	Maximum.	Minimum.	Average.	Maximum.	Minimum.	Average.
	%	%	%	%	%	%
No channel, long heating (2½ hours).	0.47	0.16	0.35	3.8	1.3	2.8
Channel, ¾ hour.....	1.92	0.05	0.65	15.4	0.4	5.2
Channel, long heating.....	2.95	0.00	0.68	23.7	0.0	5.5
Channel, long heating, high heat...	...	...	8.51	...	...	68.5
Channel, long heating, long tube.....	9.88	9.29	9.58	79.5	74.7	77.0

When the tubes were closely packed so as to insure the maximum of contact between the gases produced and the heated soda-lime (water-vapor at high temperature), and the combustion was conducted at a moderate heat and kept within the usual time of about three quarters of an hour, the full amount of nitrogen, 12.43

[1] Ztschr. anal. Chem. **24**, 1885, 448. [2] This Journal **10**, 113.

per cent. of the water-free casein, was obtained as ammonia. But when the combustion proceeded very slowly so as to occupy two and a half hours, the other conditions remaining the same, only from 12.27 to 12.08 per cent. of nitrogen were obtained as ammonia, making a loss of from 0.16 to 0.47 per cent. reckoned on the weight of the water-free casein, or from 1.3 to 3.8 per cent. of the total nitrogen. It seems reasonable to ascribe this loss to dissociation during the long time that the ammonia was exposed to the heat, though possibly some of it may have been due to incomplete ammonification of nitrogenous decomposition products. It is easy to understand how the ammonia passing rapidly through the interstices between the particles of soda-lime in the closely packed tube, in the ordinary analyses, would be so mixed with water-vapor and other gases that the nitrogenous distillation products would be completely changed to ammonia, and in the very brief exposure to heat the resultant dissociation would be too small to be noticeable. On the other hand, when the operation extends through two and a half hours instead of three quarters of an hour, it would seem by no means improbable that the anterior layer of soda-lime might, before the end of this long period during which it is kept hot, cease to give off any considerable amount of water-vapor. But it is probably this water-vapor which yields the hydrogen to form ammonia with the nitrogen of the volatile distillation products, and it is not impossible that the same vapor may also tend by its presence to prevent dissociation of ammonia. Add the fact that, when the operation goes on slowly, the time of sojourn of the ammonia in the heated tube is of course relatively much longer than the increased time of combustion would imply, and a large loss by dissociation and incomplete ammonification is easy to understand.

When a channel was left in the tube so that the contact between distillation products and soda-lime was less intimate, the loss of nitrogen was still greater. When, with the channel, the combustion occupied only three quarters of an hour, this loss varied from 0.4 per cent. to 15.4 per cent. of the total nitrogen. But when the combustion, with the channel, was prolonged to two and a half hours, the loss reached in one case 27 per cent. of the total nitrogen. This increased loss would seem most probably due to both incomplete ammonification and dissociation. At any rate, the conditions provided for less perfect contact between soda-lime and sub-

stance; for reduction of the supply of moisture which would provide hydrogen for ammonification and would also tend to prevent dissociation; and for a very long exposure of ammonia to heat.

When, with channel and long heating as before, the temperature of combustion was raised as high as the tubes would endure, the loss was very much greater and amounted to 68.5 per cent. of the total nitrogen. The most natural explanation of this increased loss is the increased dissociation of ammonia. When the length of the anterior layer of soda-lime was increased, and with it, consequently, the amount of open space inside the tube, the loss of nitrogen was greater still, namely, from 75 to 79 per cent. of the whole.

It would, of course, be foolish to attempt to say how much of the loss in these latter cases was due to dissociation and how much to incomplete ammonification. Such questions can be answered only by more detailed experiments in which the gases produced should themselves be analysed. But it does seem reasonably safe to say that both dissociation and incomplete ammonification must account for a large part, if not all, of the errors here observed, and that there is great danger of loss in these ways unless due precautions are observed.

To conclude: As regards loss by dissociation and oxidation, the facts above cited appear to warrant the inferences that, in combustions conducted by the method here described, in which (1) the tubes were so closely packed with soda-lime as to leave a minimum of free space inside, (2) full opportunity was provided for contact between distillation products and soda-lime (water-vapor at high temperature) by the anterior layer of soda-lime 12 cm. long or thereabouts, which was well heated before applying the heat to the mixture of soda-lime and substance, and maintained at a medium heat during the whole operation, and (3) the operation was completed in not over three quarters of an hour:

1. Provided the tube and contents are allowed to cool slightly before aspirating with air, there need be no loss by oxidation.

2. At a temperature sufficient to heat the tube only to dull redness, there need be no considerable loss by dissociation.

3. Ammonia may be dissociated and nitrogen lost by either very high heat, or by conducting the operation so slowly as to leave the ammonia exposed for a long time to heat. Very likely the danger of long exposure is heightened by lack of moisture

from the anterior layer of soda-lime after the latter has been heated for some time.

4. A vacant space in the tube (channel as ordinarily recommended) may involve serious loss. This loss is probably due to both incomplete ammonification of distillation products and to dissociation of ammonia.

The danger of loss of ammonia from rapid flow of the gases through the acid solution in the bulb-tube is sometimes assumed to be considerable. Musso, for instance, lays great stress upon uniform and slow evolution of gas, and prolongs the combustion for several hours, the main purpose seeming to be to insure complete absorption of the ammonia.[1] The experiments cited by Mr. Haynes in a previous article[2] imply that the real danger from this source is very small. All his attempts to push the combustion fast enough to force ammonia through the solution were ineffectual. For instance, in a combustion of sulphate of ammonia, completed in 12 minutes, the ammonia, which was sufficient to neutralise half or a little over half of the acid, was entirely absorbed. The volume of the acid solution was 10 cc.; it was contained partly in the bottom bulb and partly in the outer bulb of an ordinary Knop and Arendt bulb apparatus, in accordance with our usual practice.

Bearing of the Results upon the Interpretation of those obtained by other Experimenters. The Difficulties with the Soda-lime Method observed by Seegen and Nowack, Musso, and others.

Of the investigations which have been interpreted as casting doubt upon the reliability of the soda-lime method, those of Seegen and Nowack have perhaps been the most frequently quoted. These have carried great weight because the figures obtained were so wide of the truth despite the evident pains taken to secure accurate results, and because similarly bad results have been obtained by other chemists. The apparently unavoidable sources of serious error in the soda-lime method have been alleged as a ground for doubting the correctness of important series of researches in which the soda-lime method has been used. The question of the validity of this doubt is a very important one.

In his account of his own experiments with flesh, Nowack states that care was taken to insure uniform development of gas, and the

[1] Ztschr. anal. Chem. **16**, 414. [2] This Journal **10**, 111.

tubes were kept glowing hot for three hours ("die Röhre stets durch 3 Stunden glühen").[1] In the report of their joint experiments with animal and vegetable protein compounds, albumin, casein, syntonin, flesh, gluten, legumin, Seegen and Nowack state that they employed the same analytical methods and precautions ("die Analysen wurden in derselben Weise und mit denselben Cautelen ausgeführt, die . . . ausführlich erörtert sind") as were employed by Nowack in his own investigations just referred to.[2] The inference is that their combustions were likewise continued through a long time, if not at a high temperature. Musso, whose experiments were made with milk, whey, and cheese, says his combustions lasted hardly less than three hours, and in some cases they were prolonged for even six hours.[3] In the work of Nowack, of Nowack and Seegen, and of Musso, the figures obtained for nitrogen were very small. Taking those for nitrogen obtained by the absolute method as the standard, the loss of nitrogen in Nowack's experiments reached 20 per cent. and even more of the whole nitrogen; in those of Seegen and Nowack the loss was from 1 to 20 per cent., while in those of Musso it was over 30 per cent. of the whole nitrogen.

[1] Sitzungsber. d. Weiner Akad. **64**, Math.-Nat. Classe, II, 1871, 362. Dr. Nowack, in the article referred to, says as follows: "Weiter unterleiss ich niemals mich durch Prüfung mittelst sehr empfindlicher rother und blauer Lackmuspapiere von der genauen Neutralisation zu überzeugen, da bei einer noch so langsamen geleiteten Verbrennung von Fleisch mit Natronkalk die Will-Varrentrapp'sche Vorlage durch die entstandenen Distillationsprodukte sich derart färbt dass das Betüpfen eines sehr empfindlichen Lackmuspapieres das Erkennen der Neutralisationsgrenze viel deutlicher anzeigt, als die Beobachtung der Endreaction in der missfarbigen Flüssigkeit. . . . Bei der Ausführung der Verbrennung mittelst Natronkalk sorgte ich für den regelmässigen Gang der Gasentwickelung, liess die Röhre stets volle drei Stunden glühen, steigerte namentlich in der zweiten Hälfte der Verbrennungsdauer die Hitze so hoch als möglich und endete nicht früher als bis der Natronkalk Spuren von Schmelzung zeigte, und an seiner Oberfläche keine schwärzlichen Kohlenpartikeln mehr, sondern nur eine graulichweisse Farbe wahrnehmbar war."

The article by Dr. Nowack, from which the above is cited, was preceded by one by Prof. Seegen (loc. cit., II, 63, 11), "Zur frage über die Ausscheidung des Stickstoffs der im Körper zersetzten Albuminate," in which he says the nitrogen was determined in flesh by elementary analysis with copper oxide and "durch Glühen mit Natronkalk in dazu vorbereiteten, starken, etwa ½ Meter langen Verbrennungsröhren." The results with soda-lime were all lower than the lowest with copper oxide. That the nitrogen was not all converted into ammonia Prof. Seegen shows by the fact that "als ich den Glührückstand mit Wasser verrieb und das Ganze neuerdings der Glühhitze unterzog, es wurden beim zweiten Glühen stets noch grössere oder geringere Mengen von NH_3 in der Will'schen Vorlage nachgewiesen, und ausserdem zeigte der zweite Glührückstand einen ganz exquisiten Geruch nach Methylamin." On another page Prof. Seegen says that Dr. Nowack had made a number of nitrogen determinations in flesh, which were to be published later, referring, evidently, to those in the article by Dr. Nowack, above cited; and adds, "Die Arbeit ist mit grösster Sorgfalt, mit Beobachtung aller Cautelen und Berücksichtigung jeder Fehlerquelle ausgeführt."

[2] Pf. Archiv. **7**, 1873, 290.

[3] Ztschr. anal. Chem. **16**, 1877, 414.

On the other hand, Gruber, who in reply to the criticism of Seegen and Nowack upon analyses by Voit and others in Munich, gives very satisfactory results obtained in Voit's laboratory with protein in flesh, never allowed more than an hour for the combustions.

The experiments cited by Mr. Woods and myself in article No. IV of this series seem to us to give satisfactory assurance of the reliability of soda-lime determinations of nitrogen in ordinary protein compounds when the combustions were made with proper precautions. Of the latter the chief seem to us to be (1) sufficiently fine pulverisation and careful mixture of the substance with soda-lime; (2) close packing of the tube and sufficiently long anterior layer of soda-lime, so as to insure sufficient contact between soda-lime (heated water vapor) and distillation products, as well as to avoid too long sojourn of ammonia in the heated tube; and (3) maintaining the anterior layer at a moderate heat during the whole time of combustion, which should not be too protracted.

Messrs. Seegen and Nowack do not state whether they left a channel in their tubes or not, but it is evident that the conditions of their work were such as to favor incomplete decomposition of the nitrogenous substance, imperfect ammonification of volatile decomposition products, and dissociation of ammonia. Prof. Seegen reports a nitrogenous residue in the tube after the combustions, and Dr. Nowack found the acid solutions in the nitrogen bulbs so highly colored as to interfere with titration with litmus solution. The combustion was prolonged for three hours and during part of this time at a very high heat. The determinations of Muss were conducted very slowly, in some cases even more so than those of Seegen and Nowack, and the results obtained were likewise very low. Mr. Ball and I found that either leaving a channel in the tube, or high heating, or prolonging the combustion to two and a half hours, involved large loss of nitrogen, the loss with these conditions combined amounting, in some cases, to two thirds or three fourths of the whole nitrogen.

It would seem, therefore, that we have here cases of a kind not unfrequent in scientific research, in which the very effort to secure correct and reliable results involves grievous error.

I lay especial stress upon this matter because of the use that has been made of Seegen and Nowack's results to discredit the soda-lime method in general, and particularly to throw doubt upon the

work of Voit and others in the Physiological Laboratory at Munich, in which this method has been employed in the study of the fundamental problems of nutrition. It was my fortune some time since, while working in that laboratory, to be permitted to observe very closely the ways in which determinations of nitrogen by soda-lime are there conducted. Although the effort to insure close packing of the tubes was perhaps less than in the experiments above detailed, and upon which the conclusions here given are based, yet on the whole the details of manipulation as I observed them were such as would, with the experience in this laboratory, lead one to expect correct results.

Although the results of experiments by Gruber and others in the Munich laboratory, and accumulated experience elsewhere, make any vindication of its work superfluous, yet I trust these statements, in connection with an explanation of the error into which Seegen and Nowack have unwittingly fallen, may, in the interests of science, not seem out of place.

The experience of other chemists, as well as that in this laboratory, of which part has been described in these pages, leaves me with the decided belief that the Scylla and Charybdis of the soda-lime determination are incomplete ammonification of nitrogenous distillation products and dissociation of ammonia. The other difficulties are, in general, easy to overcome. They may all be prevented, in ordinary animal and vegetable protein compounds, by the precautions above enumerated. But in alkaloids and allied compounds, and in some amines, and amido and azo-compounds, loss by incomplete ammonification seems very difficult to avoid.

The observations I have had occasion to make, as well as printed accounts of the methods followed in different laboratories, have given me the decided impression that the most common difficulties are loose packing of the combustion tube so as to leave a channel, insufficient anterior layer of soda-lime, and too high or too long-continued heating.

The soda-lime method is beset with dangers and requires great care to avoid them. Indeed, after the experience in this laboratory, covering a period of several years and including some thousands of nitrogen determinations, if I were going to undertake again a series of analyses like those for which these studies were made, and the details of the work were to be placed in the hands of an analyst, however expert, who had not been through some such

experience as that above described, I should feel under the necessity of asking him to do a considerable amount of preliminary work, including comparison of results by the soda-lime with other methods, before I could feel sure of his results. A case in point may be worth mentioning.

After most of the above detailed experiments had been made and we had the method in such control that we were wont to say jocosely that from a given protein compound we could obtain the whole or any desired fraction of the nitrogen as ammonia, at will, a gentleman of no little experience, and who afterwards proved himself a skillful and efficient analyst, came to our laboratory as assistant. We placed a number of substances, mostly animal tissues, in his hands for nitrogen determinations by the soda-lime method, instructing him in the details of the process, and going through a number of determinations with him. He was very confident that he could secure perfectly reliable results and at the same time make the determinations with considerable rapidity. After a list of substances had been analysed I looked over his figures and was somewhat surprised at the variations in the duplicate determinations, which in some cases, as I now recall, reached nearly 0.2 per cent. This led me to question their accuracy. Mr. Woods, by whom most of the nitrogen determinations of this investigation have been made, repeated the analyses and found in almost every case a considerably higher percentage of nitrogen, so that the whole work had to be repeated. The most plausible explanation of the errors seemed to be that the determinations in question were made rather hurriedly, and either because the nitrogenous material was not well enough mixed with the soda-lime, or from too loose packing of the tube, some of the nitrogenous distillation products were incompletely ammonified and thus escaped detection in the titration subsequent to combustion.

At the same time I must repeat what I have already said, that our experience leads me to place the greatest confidence in the soda-lime method for the determination of nitrogen in ordinary protein compounds, provided the work be conducted with the precautions here insisted upon.

The perfection to which Kjeldahl's method has lately been brought, and its accuracy, convenience, and inexpensiveness, have led to its use in this as in many other laboratories. Our experience leads us to decidedly prefer it to the soda-lime method, though we find it advantageous to use both, making one check the other.

But the danger of incomplete ammonification of some classes of compounds, *e. g.* alkaloids, makes us feel it necessary to control both by the absolute method for all classes of substances except those for which they have been most thoroughly tested.

Summary.

The experimental and other considerations presented in this and the previous articles on the determination of nitrogen by soda-lime, may be conveniently summarised, after first recalling the probable reaction by which the nitrogen is changed to ammonia, and the principal sources of error in the operation.

1. It seems decidedly probable that the change of nitrogen to ammonia is effected by union, at high temperature, with water vapor yielded by the soda-lime (or slaked lime in case the latter is used). It is essential that the contact between nitrogenous distillation products and water vapor be sufficient and at not too high or too low temperature to insure conversion of all the nitrogen to ammonia, and that the ammonia be not dissociated or oxidised. The main objects, then, are to secure complete ammonification and to avoid dissociation and oxidation.

2. The chief difficulty in the way of complete ammonification of protein compounds appears to be the formation of gases which do not readily yield their nitrogen to be united with the hydrogen of the water vapor. With certain other classes of nitrogenous compounds, as leucine and its congeners, alkaloids, amines, and amido and azo-compounds, this difficulty is greater and sometimes apparently insuperable. The tendency of protein compounds to be decomposed by heat and other agencies into leucine, amines, etc., appears to explain the difficulty frequently found in getting all their nitrogen into the form of ammonia by heating with soda-lime. The evident means to secure complete ammonification must be sufficient contact with soda-lime at proper temperature.

3. The danger of dissociation of ammonia evidently increases with increase of temperature and time of exposure, and is probably diminished by presence of water vapor and other diluting gases. If this be so, the danger will be avoided by measurably rapid combustion at not too high heat, and by keeping the ammonia in contact with sufficient moisture from the soda-lime until it leaves the heated tube.

4. Leaving out of account substances such as nitrates, nitro-compounds, etc., whose nitrogen is imperfectly converted into

ammonia by soda-lime, even in the presence of organic matter, and assuming palpable errors of manipulation to be avoided, such as (*a*) loose packing of asbestos plug, which would allow particles of soda-lime to be swept into the acid bulb; (*b*) heat at anterior end of the tube so low as to permit ammonia to be retained with moisture about the cork, or so high as to char the cork and give rise to acid or alkaline distillation products; (*c*) use of soda-lime containing nitrates or nitrites, which may, according to circumstances, either furnish nitrogen to be transformed into ammonia or oxygen to burn the ammonia formed from the nitrogen of the substance; (*d*) use of distilled water containing ammonia for rinsing the acid bulb; (*e*) imperfectly cleaned or incorrectly calibrated burettes; the principal sources of error above discussed involve loss of nitrogen, and may be recapitulated thus:

I. Loss from imperfect ammonification of the nitrogenous substance, due to:—

a. Incomplete decomposition of the substance, part of the nitrogen being, from coarseness of the particles of the substance, imperfect mixing with the soda-lime, insufficient heat, or other cause, left behind in the charred residue.

b. Change of nitrogen into compounds other than ammonia, either such as may remain in the tube, *e. g.* cyanogen; or volatile distillation products which escape ammonification and pass through the acid solution unabsorbed, or, if absorbed, are not accurately determined by the titration or other means used to find the amount of nitrogen in the solution.

c. Escape of nitrogen in the free state.

II. Loss of ammonia through:—

a. Dissociation at high heat in the combustion tube.

b. Oxidation by air present in the tube before, or introduced in aspirating to wash out ammonia after, the combustion.

c. Neutralisation by acid products, *e. g.* of sugar, where the latter is used in the combustion.

d. Incomplete absorption by the acid solution.

5. Complete decomposition of the substance has, in our experience, been readily secured by pulverisation fine enough for it to pass through a sieve of 1 mm. aperture; thorough mixing with soda-lime; avoiding the shaking by which the particles gather at the top of the soda-lime; and heating to low redness.

6. With sufficient soda-lime, not too dry, we have found no reason to fear the formation of cyanides, nor have we been able

to obtain any indication of the escape of free nitrogen when the operation is properly conducted, although it might, perhaps, occur by oxidation of ammonia if there were nitrates or nitrites present, or if aspiration with air were done while tube and contents are hot. Turning off the flame before aspirating has, in our experience, sufficed to avoid oxidation by air. At least, if ammonia has been oxidised, the quantity has been too small to be detected.

7. When sugar is used, acid products may be formed in quantities large enough to impair the accuracy of the determinations. With ordinary animal and vegetable protein compounds, provided enough soda-lime is employed, the use of hydrogen, or sugar, or other substances for supplying gases, either to expel air, or to yield nascent hydrogen to form ammonia with the nitrogen, or to dilute the ammonia and prevent dissociation, or to wash out the ammonia, appears to be unnecessary. The danger of loss by incomplete absorption of the ammonia by the acid solution appears to be very small indeed, even when the development of gases is very rapid, provided sufficient acid solution be used.

The chief sources of loss appear to be from incomplete ammonification and from dissociation of the ammonia formed.

8. The first of these two difficulties is a serious one. With protein compounds, the great trouble is evidently the formation of volatile decomposition products which do not readily yield their nitrogen to form ammonia with hydrogen. This is easy to understand when we consider that protein compounds are prone to yield cleavage products such as leucine and its congeners, compounds allied to the alkaloids, amido-compounds, etc.; and that it is very difficult to get all the nitrogen of these latter into the form of ammonia with soda-lime, evidently because of their proneness to form compounds that resist the ammonifying action.

With alkaloids and allied compounds, leucine and other amido-compounds, amines, and azo- and nitro-compounds, complete ammonification is not always effected even with the utmost care. Concerning peptones our experience does not enable us to speak. But for the protein of ordinary animal and vegetable substances, including casein, proper precautions appear to insure complete ammonification of the nitrogen. The important condition appears to be sufficient contact with heated soda-lime (*i. e.* with water vapor at high temperature).

This contact is best secured by (*a*) intimate mixture of substance with soda-lime; (*b*) close packing so as to avoid open space inside

the tube; (*c*) providing a reasonably long anterior layer of soda-lime; (*d*) heating this latter to dull redness before bringing the heat to bear upon the substance, and keeping it hot until the combustion is done. In order to insure the maximum of surface for contact it is well to have the anterior layer consist of coarse particles of soda-lime containing enough lime to prevent fusing together. It is possible that too long heating may result in expelling the water from the soda-lime, so that there will not be enough in the latter part of the operation to insure complete ammonification.

Though it is desirable to avoid coloration and turbidity of the acid solution, these do not necessarily imply incomplete ammonification, nor does their absence prove perfect combustion. With proper care to insure contact between soda-lime and substance, we have almost never found the solution so colored as to seriously interfere with titration.

9. Ammonia may be dissociated and nitrogen lost by either too high heating, or by conducting the operation so slowly as to leave the ammonia exposed for a long time to heat. It seems probable that the presence of water vapor, as of other gases, would tend to prevent dissociation of the ammonia, and that the danger of long heating may be partly due to reduced supply of moisture from the anterior layer of soda-lime after the latter has been heated for some time.

10. A vacant space in the tube (channel as ordinarily recommended) may cause serious loss. This loss is greater the higher the temperature and the longer the time of combustion. It is probably due not only to incomplete ammonification of distillation products through lack of contact with the soda-lime, but also to dissociation of ammonia. With the channel the flow of the gases is slower and they are exposed to heat longer than when the tube is packed full. Add the possible lack of water vapor when the heating is long continued and the loss by dissociation is very clearly explained. When the tube is closely packed, the flow of gases reasonably fast, and the operation conducted at a temperature sufficient to heat the tube only to dull redness, there appears to be no considerable loss by dissociation, even with a long anterior layer (20 or 30 cm.) of soda-lime.

Concerning reagents, apparatus and manipulation, a few words will suffice.

1. *Soda-lime.*—The soda-lime made by mixing one part of ordinary caustic soda with two and a half parts of quicklime by the process described,[1] costs very little for materials and labor, and serves the purpose very satisfactorily. In sifting it is conveniently divided into a finer portion to be mixed with the substance, and into coarser particles to be used for the anterior layer. It bears heating without fusing so much as to leave any considerable open space in the tube if closely packed at the outset. Varying proportions of soda-lime, from 1 part to 2½ parts of lime to each part by weight of soda, have made no difference in the results of the analyses. We have obtained equally good results with the mixture of sodium carbonate and slaked lime as described by Johnson, and see no reason why slaked lime as recommended by him should not be generally efficacious as it has proven in the cases cited by him and in those tried by ourselves. Our reason for adhering to the ordinary soda-lime has been the impression that by filling the anterior portion of the tube with coarse particles of the rather difficultly fusible material, more complete contact is insured between nitrogenous distillation products and the heated water vapor from the soda-lime. The old theory that enough soda should be mixed with the lime to make the mixture easily fusible does not stand the test of experience.

In testing the purity of soda-lime by sugar, as is sometimes recommended, there is danger of error both from the presence of nitrogen in the sugar and from formation of acid distillation products.

2. *Tubes and charging.*—For ordinary combustions, tubes of from 35 to 40 cm. in length do very well. The method of charging the tube upon which we have gradually settled after numerous trials with tubes of different lengths and charged in different ways, is explained in the accompanying tabular statement:

Length of tube	40 cm.
Asbestos and fine soda-lime . . .	4 "
Mixture, fine soda-lime and substance .	16 "
Rinsings, fine soda-lime . . .	4 "
Anterior layer, coarse soda-lime . .	12 "
Asbestos, open space, plug . . .	4 "

With a shorter tube the divisions may be made proportionately shorter. We intend to have at least 40 parts by weight of fine

[1] This Journal **9**, 312.

soda-lime for every part of substance in the "mixture." About 0.4 and 0.6 of flesh (water free), or corresponding amounts of other materials, we find convenient. The importance of fine pulverisation of substance, intimate mixture with soda-lime, filling the tube compactly so as to have no channel, avoiding the shaking by which particles of the substance might be brought to the top of the soda-lime, and heating until no charred material is left, has been dwelt upon. An anterior layer of coarse soda-lime, 12 centimeters long, has proven very satisfactory. The anterior layer should be well heated before the heat is applied to the mixture of soda-lime and substance, and kept hot until the combustion is done.

3. *Heat and time of combustion.*—A "low red" heat ordinarily suffices. Heating to bright redness brings danger of loss of ammonia by dissociation, though in our experience, when the tube is closely packed and the operation not too slow, we have found practically no difficulty in getting all the nitrogen as ammonia even at high heat. But with a channel in the tube the loss by high heating has been considerable.

Ordinarily, three quarters of an hour is ample for the combustion, and an hour the extreme limit, according to the experience in this laboratory. Rapid combustion is less and long heating more dangerous than is frequently taught. With an ordinary Knop and Arendt (four bulb) bulb apparatus containing 10 cc. of acid solution, of which little over half was required to neutralise the ammonia, the ammonia was completely absorbed even when the combustion lasted only twelve minutes. Serious loss may result from too long heating, especially if there be open space in the tube or the temperature is high.

4. *Determination of the ammonia.*—In the combustion of ordinary protein compounds with the precautions stated above, practically all the nitrogen is converted into ammonia, and its determination by titration is easy. We find it well, however, to use concentrated solutions and to avoid excess of water in rinsing out the bulbs. The quantity of concentrated acid solution required is small and the tension in the combustion tube during the heating consequently slight, which is a convenience; while, with the small quantity of solution in titrating, the color reaction is sharp and the determination easy and accurate. Freshly prepared cochineal solution is the most satisfactory indicator we have found. Very narrow burettes, in which 10 cc. occupy from 30 to 40 cm., have decided advantages for convenience and accuracy when concentrated solutions are used.

Contributions from the Chemical Laboratory of Harvard College.

LIX.—ON TRIBROMTRINITROBENZOL.[1]

By C. Loring Jackson and John F. Wing.

The following paper contains the description of the first results of a research on tribromtrinitrobenzol and its derivatives, which we are obliged to publish now, as on account of the departure of one of us from Cambridge we cannot go on with the work together. Had it not been for this, we should have postponed its publication until our experiments on the reduction of triamidotrinitrobenzol had led to some definite result. At present we are able to describe only the tribromtrinitrobenzol, triamidotrinitrobenzol, and trianilidotrinitrobenzol, with several preliminary experiments on other substances which we mention in order to reserve the further study of this subject for one of us, who will continue it in this laboratory.

The tribromtrinitrobenzol has never been described, for although Koerner[2] in 1874 stated that he had obtained it by the action of a mixture of boiling fuming nitric and sulphuric acids on tribromdinitrobenzol, he gave no description of it, saying that this must be postponed till a later paper. Some years afterward (in 1879) Wurster and Beran,[3] after many attempts to prepare the substance according to Koerner, came to the conclusion that it could not be made in this way, as, even when Koerner's mixture of acids was heated with tribromdinitrobenzol to 220° in a sealed tube, they got only a very small amount of a substance melting from 200° to 220°, the greater part of the product being unaltered tribromdinitrobenzol. As this paper has remained unanswered by Koerner up to the present time, that is, for eight years, we have assumed that he has abandoned the subject, and have accordingly taken it up, our attention being called to it by the results obtained in the study of the action of nitric acid on trichlorbenzol described in a previous paper.[4] Upon treating symmetrical tribrombenzol with a mixture of fuming sulphuric acid and a nitric acid of specific gravity 1.51, but essentially free from nitrous fumes, we found, as

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] Gazz. chim. ital, 1874, 425.

[3] Ber. d. chem. Ges. **12** (1879), 1821.

[4] This Journal **9**, 348.

stated in the paper just mentioned, that tribromtrinitrobenzol was formed, thus confirming the results of Koerner, in opposition to those of Wurster and Beran; and in the same place we have tried to show that the most probable cause of the failure of these latter chemists to obtain tribromtrinitrobenzol was the presence of a large quantity of nitrous fumes in the nitric acid used by them, which raised its specific gravity without increasing its strength.

Tribromtrinitrobenzol, $C_6Br_3(NO_2)_3$.

Symmetrical tribrombenzol (melting point 119°) was converted into tribromdinitrobenzol, either by treatment with nitric acid[1] of specific gravity 1.51, the mixture being warmed to secure complete action, or by boiling it with a mixture of commercial fuming nitric acid and common sulphuric acid. To convert the tribromdinitrobenzol, by whichever process prepared, into tribromtrinitrobenzol, 20 grams of it were dissolved by the aid of heat in a mixture of about 500 cc. of the nitric acid of specific gravity 1.51 mentioned above with one third of its volume of fuming sulphuric acid, since these proportions had been found by experiment to give the best result with the least consumption of acid, and the solution boiled gently in a flask loosely closed with a glass bulb. As a portion of the nitric acid volatilises during the boiling, a little of the solid separates, which can be dissolved by the addition of more nitric acid, but this precaution is not necessary in working on a large scale. When the mixture had boiled for four to five hours it was allowed to cool, and then, disregarding the comparatively large amount of solid which had separated, poured into snow, and the precipitate washed thoroughly with water and afterward purified—first by extraction with hot alcohol, which removed the unaltered tribromdinitrobenzol, since the tribromtrinitrobenzol is but slightly soluble even in hot alcohol—and then by crystallisation from chloroform, which separated the less soluble tribromtrinitrobenzol from the tetrabromdinitrobenzol[2] which was always formed at the same time. The crystallisation from chloroform was continued until the substance showed the constant melting point of 285°; it

[1] Prepared directly from sulphuric acid and nitre, not pushing the reaction beyond the formation of acid potassic sulphate. See our previous paper, this Journal **9**, 348.

[2] The purification and identification of this substance are described at the end of this paper. If the tribromtrinitrobenzol is to be used in making triamidotrinitrobenzol it is not necessary to purify it completely from tetrabromdinitrobenzol.

was then dried at 100°, and its composition determined by the following analyses:[1]

I. 0.2310 gram of the substance gave 19.6 cc. of nitrogen under a pressure of 765 mm. and a temperature of 21°.

II. 0.1688 gram of the substance gave, according to the method of Carius, 0.2128 gram of argentic bromide.

	Calculated for $C_6Br_3(NO_2)_3$.	Found. I.	II.
Nitrogen	9.33	9.72	
Bromine	53.33	...	53.64

The yield was far from satisfactory, amounting on the average from about 15 to 20 per cent. of the theoretical, although on one occasion we obtained 40 per cent. As, however, the tribromdinitrobenzol used in this case was the residue from the alcoholic extracts derived from previous preparations, we think that a considerable part of this large yield consisted of tribromtrinitrobenzol from the previous processes, which had been dissolved by the hot alcohol, since, although nearly insoluble in hot alcohol, it is not completely so. It follows from this that it is well to use the tribromdinitrobenzol obtained in purifying the crude product with alcohol as material for a new preparation.

Properties.—The tribromtrinitrobenzol forms good-sized, well developed white crystals, with perhaps a slight yellowish tinge, which differ in habit according to the solvent from which they have been crystallised. From benzol, hexagonal prisms terminated by hexagonal pyramids are deposited, which look very much like some forms of quartz crystal; from a mixture of benzol and alcohol, long, slender, tapering prisms are obtained, which under the microscope seem to be made up of rows of hexagonal pyramids united as in cap quartz, so that the edges of the prisms are bluntly serrated; crystallised from chloroform, the prisms are not so slender as from benzol and alcohol, and the twinning just described is much better marked. These crystals, furrowed by numerous re-entering angles parallel to the basal plane, are very characteristic. The substance melts at 285° (uncorr.), and sublimes to a slight extent when heated in an air-bath, even at as low a temperature as 175°. It is but slightly soluble in alcohol, even when boiling, essentially insoluble in it when cold, soluble in chloroform, and more easily in ether, benzol, acetone, glacial acetic acid, or

[1] See also page 287.

carbonic disulphide. Chloroform, or a mixture of benzol and alcohol, is the best solvent for it.

The tribromtrinitrobenzol is a decidedly reactive substance, forming compounds with most of the common reagents; of these compounds we have been able to study thoroughly only those derived from alcoholic ammonia and aniline, which will be described later in the paper, but some preliminary experiments with other reagents may find a place here. With potassic hydrate, dissolved in alcohol, a yellow product was formed which gave red potassium and yellow barium salts, the latter being only slightly soluble, and separating in hair-like crystals from its hot aqueous solution. It is probable that this product is the trinitrophloroglucine of Benedikt,[1] but to decide this point the experiment must be repeated with a larger quantity of substance. With sodic ethylate it gives what appears to be a new compound. When boiled with an alcoholic solution of potassic sulphocyanate it forms a dark red powder, which we have not yet succeeded in obtaining in crystals. When heated in a sealed tube with potassic iodide and alcohol to 150° for 18 hours, a crystalline compound is formed which has a very high melting point and explodes when heated to a somewhat higher temperature; but the yield is so small that we have not been able as yet to obtain enough of it sufficiently pure for analysis. All these substances will be more thoroughly studied in this laboratory, and the behavior of tribromtrinitrobenzol with other reagents, especially sodium malonic ester, will be investigated also. When tribromtrinitrobenzol is heated to 100° with common strong sulphuric acid, it dissolves, but crystallises out unaltered as the solution cools. A boiling solution of argentic nitrate in alcohol has no action on it, and the same remark applies to argentic nitrite, as was to be expected. We hope, however, that the triiodtrinitrobenzol may react with this latter substance, and it was for this reason that we undertook the study of the action of potassic iodide on the tribromtrinitrobenzol.

In the hope of obtaining addition products similar to those formed by Hepp's trinitrobenzol with hydrocarbons, we have studied the action of tribromtrinitrobenzol on naphthaline. For this purpose benzol solutions of the two substances were mixed in the proportion of one molecule of each, but we obtained from the mixed solutions only crystals melting at 285°; as, however, the

[1] Ber. d. chem. Ges. **11**, 1376.

melting tubes contained a slight sublimate, and the habit of the crystals was somewhat different from that of tribromtrinitrobenzol, we thought it possible, although not probable, that a compound might have been formed which decomposed before it melted, and have accordingly analysed the crystals, which, remembering the instability of Hepp's substance, were dried only by pressing between filter paper, in order to be certain that the substance should not be decomposed.

0.1200 gram of the substance gave, according to the method of Carius, 0.1500 gram of argentic bromide.

	Calculated for $C_6Br_3(NO_2)_3$.	Found.	Calculated for $C_6Br_3(NO_2)_3C_{10}H_8$.
Bromine	53.33	53.20	41.52

It is evident, therefore, that the substance is only tribromtrinitrobenzol, and that it does not combine with naphthaline under these conditions. The same negative result was obtained when chloroform or ether was substituted for benzol as the solvent. We may add, too, that the tribromtrinitrobenzol shows no tendency to unite with benzol, so far as we could find.

Triamidotrinitrobenzol, $C_6(NH_2)_3(NO_2)_3$.

When tribromtrinitrobenzol is mixed with cold alcoholic ammonia, an action sets in almost immediately, as shown by the appearance of an orange color in the solution; and, if the substances are allowed to stand for twelve hours in a corked flask at ordinary temperatures, the reaction proceeds further, but is not complete, as is shown by the presence of white specks consisting of unaltered tribromtrinitrobenzol in the undissolved solid. It is necessary, therefore, in order to bring this small amount of unaltered substance into the reaction, to boil the mixture in a flask with a return condenser for about half an hour, adding more alcoholic ammonia as it is needed. The nearly insoluble triamidotrinitrobenzol is then filtered hot from the orange liquid, which has the color of a strong solution of potassic dichromate,[1] and the paler yellow solid purified by washing, first with water to remove ammonic bromide, and afterward with alcohol to get rid of the organic impurities.

The triamidotrinitrobenzol can be made conveniently also from the mixture of tribromtrinitrobenzol and tetrabromdinitrobenzol

[1] Our study of the substances contained in this liquid is not complete as yet, but a description of the results obtained up to this time will be found on page 290.

obtained in purifying tribromtrinitrobenzol, thus utilising directly a secondary product which could be separated into its pure constituents only with a great outlay of time and work. For this purpose the mixture is treated with alcoholic ammonia in the manner already described when speaking of the preparation from pure tribromtrinitrobenzol, and the product freed from the tetrabromdinitrobenzol, which is not attacked by alcoholic ammonia under these conditions, by boiling and washing with benzol or chloroform after the washing with alcohol.

The composition of the substance after being dried at 100° was determined by the following analyses:

I. 0.2352 gram of the substance gave on combustion 0.2370 gram of carbonic dioxide and 0.0544 gram of water.

II. 0.2346 gram of the substance gave 0.2342 gram of carbonic dioxide.[1]

III. 0.2186 gram of the substance gave 60.4 cc. of nitrogen under a pressure of 770 mm. and a temperature of 19°.

IV. 0.1058 gram of the substance gave 29.6 cc. of nitrogen under a pressure of 765 mm. and a temperature of 20°.

	Calculated for $C_6(NH_2)_3(NO_2)_3$:	Found. I.	II.	III.	IV.
Carbon	27.90	27.48	27.23		
Hydrogen	2.32	2.57			
Nitrogen	32.55	...	...	32.19	32.22

Properties.—As obtained from the action of alcoholic ammonia on the tribromtrinitrobenzol, the triamidotrinitrobenzol forms an amorphous powder of an orange or yellow color, according to the conditions under which it was prepared; crystallised from aniline or nitrobenzol, it forms small rhombic plates of a pale yellow color. It decomposes without melting above the boiling point of mercury, and is nearly, although not completely, insoluble in water, alcohol, ether, benzol, chloroform, or glacial acetic acid. It dissolves in aniline, or in nitrobenzol, and, as already stated, can be obtained in crystals from these solutions. Cold strong sulphuric acid slowly dissolves it, forming a pale yellow solution, but on dilution the unaltered substance is precipitated. Dilute sulphuric acid, or dilute or strong nitric or hydrochloric acid, has no action on it, and when the substance was suspended in alcohol and hydrochloric acid gas passed into the liquid no change was observed. It is therefore

[1] The hydrogen of this analysis was lost.

either incapable of forming salts, or can form them only under unusual conditions. When the solution in strong sulphuric acid was heated it became charred.

We have made many attempts to convert the triamidotrinitrobenzol into an acet-compound, but have found that it was not acted on by glacial acetic acid, acetylchloride, or acetic anhydride, even when sealed with the substance and heated to 150°; we infer, therefore, that the radical acetyl cannot be introduced directly into the molecule.

The reduction of triamidotrinitrobenzol naturally has engaged our attention, as by this means it might be possible to obtain hexamidobenzol. Owing to want of material, however, our experiments on this subject have not been brought to a conclusion, but we think it best to describe them briefly now, as we shall have no other opportunity to put them in print, if the future work of one of us on this subject should not lead to the desired result; and there seems to be only too much reason to fear that this will be the case, especially since Nietzki and Hagenbach[1] have found that ammonia is eliminated in reductions which should lead to pentamidobenzol. Up to this time we have tried only three reducing agents, tin and hydrochloric acid, ammonic sulphydrate in alcoholic solution, and zinc dust and acetic acid. The first of these, tin and hydrochloric acid, removed ammonia from the molecule, as was proved by the formation of pink salt and the precipitation of ammonic chlorplatinate on adding chlorplatinic acid, the latter being analysed for still greater certainty. This was the result whether tin and hydrochloric acid or stannous chloride and hydrochloric acid were used. The alcoholic solution of ammonic sulphydrate gave a more promising result; but, as it was evident that the product was decomposed at a temperature a little above that at which it was formed, we turned our attention to the third method, which seemed on the whole the most promising, since zinc dust and 80 per cent. acetic acid acting in an atmosphere of carbonic dioxide seem to reduce the triamidotrinitrobenzol completely; at any rate the yellow color disappears and the whole goes into solution. This solution, after being freed from zinc with sulphuretted hydrogen, gave no precipitate with sodic hydrate, nor did ether extract anything from the alkaline solution. It was blackened by exposure to the air even more readily than a solution of a salt of diamido-

[1] Ber. d. chem. Ges. **20**, 331. See also p. 2114.

benzol, and the residue from it was decomposed easily by heat; chlorplatinic acid gave no precipitate with it, but chlorauric acid threw down an uninviting precipitate which we thought was in part at least a product of oxidation. If the substance formed was really hexamidobenzol, it is evident that its isolation in a form fit for analysis will be a matter of great difficulty owing to its extreme instability. The study of this subject will be continued in this laboratory, however, as soon as a sufficient quantity of material can be prepared, and the work will be extended also to the action of other reducing agents, including those which form azo-compounds.

As yet we have been unable to finish the study of the substances contained in the orange-red filtrate formed in the preparation of the triamidotrinitrobenzol, because, in spite of its marked color, the amount of solid dissolved in it is far from large. It seems, however, to contain at least two compounds, one crystallising in red needles, frequently grouped in round masses like chestnut burs, the other a yellow substance forming flat crystals; but the separation of these two bodies is a matter of such great difficulty that we have not yet succeeded in obtaining either of them in a state of purity, nor are we certain that these are the only secondary products of the reaction.

Trianilidotrinitrobenzol, $C_6(NHC_6H_5)_3(NO_2)_3$.

This substance was prepared by allowing a mixture of tribromtrinitrobenzol and aniline, in the proportion of one molecule of the former to six of the base, to stand at ordinary temperatures, when the reaction runs slowly, but is complete after the mixture has stood for a day or two. The product was purified by washing with water to which a little hydrochloric acid was added to remove any slight excess of free aniline, and crystallising the residue from a mixture of alcohol and chloroform. It was dried at 100°, and analysed with the following results:

I. 0.1468 gram of the substance gave on combustion 0.3176 gram of carbonic dioxide and 0.0516 gram of water.

II. 0.1830 gram of the substance gave 28.1 cc. of nitrogen at 25° temperature and 755 mm. pressure.

	Calculated for $C_6(NHC_6H_5)_3(NO_2)_3$.	Found. I.	II.
Carbon	59.26	58.99	
Hydrogen	3.71	3.90	
Nitrogen	17.28	...	17.02

If an excess of aniline is used in the preparation and the mixture heated, a coloring matter is formed looking like rosaniline; but the purification of this substance was attended with such great difficulties that we have abandoned for the present the further study of this reaction, in which the nitro groups undoubtedly play a part.

Properties.—The trianilidotrinitrobenzol forms an orange powder, crystallising from alcohol or chloroform in fine red needles which melt at 238°. It is essentially insoluble in water, soluble with difficulty in alcohol, but easily in chloroform, soluble in ether, benzol, glacial acetic acid, or acetone. The best solvent for it is a mixture of alcohol and chloroform. Hydrochloric acid has no action on it, and in general it shows no more tendency to form salts than the corresponding amido compound. Strong nitric acid produces no change of color when added to it.

Tetrabromdinitrobenzol, $C_6Br_4(NO_2)_2$.

As has been already stated, during the preparation of the tribromtrinitrobenzol from tribromdinitrobenzol by the action of nitric acid and fuming sulphuric acid there was formed invariably another substance which melted in the crude state at about 230°, and was left behind with the tribromtrinitrobenzol after the tribromdinitrobenzol was removed with alcohol, and was separated partially from it by crystallising the residue from chloroform, in which the trinitro compound is less soluble than the other substance. In this way it is easy to get the trinitro compound in a state of purity; but to purify completely the other substance it is necessary to submit the residue from the evaporation of the chloroform mother-liquors to systematic fractional crystallisation from a mixture of alcohol and benzol, which removes a small quantity of tribromtrinitrobenzol. These crystallisations lowered the melting point instead of raising it, as is usual, and after it had been brought down from about 230° to 224° it remained constant, and then the substance, dried at 100°, was analysed with the following results:

I. 0.3526 gram of the substance gave 18.7 cc. of nitrogen at 24° temperature and 764 mm. pressure.

II. 0.1690 gram of the substance gave, by the method of Carius, 0.2606 gram of argentic bromide.

	Calculated for $C_6Br_4(NO_2)_2$.	Found. I.	Found. II.
Nitrogen	5.78	5.97	
Bromine	66.11	...	65.62

These analyses and the melting point 224° prove that the substance is the tetrabromdinitrobenzol, melting point 227°–228°, discovered by von Richter.[1]

The following experiments were tried to throw light upon the manner in which the tetrabromdinitrobenzol was formed. In the first place, to prove that it was not formed from an impurity (tetrabrombenzol) in our tribrombenzol, we have prepared it from an analysed sample of tribromdinitrobenzol. This experiment was hardly necessary, as the tribrombenzol and tribromdinitrobenzol used by us in working on the large scale showed the correct melting points within two degrees; but we felt that absolute certainty on this point was important, and accordingly prepared some perfectly pure tribromdinitrobenzol, melting point 190° (von Richter[2] gives 191°, Koerner[3] 192°), which gave on analysis the following result:

0.1658 gram of the substance gave, according to the method of Carius, 0.2314 gram of argentic bromide.

	Calculated for $C_6Br_3(NO_2)_2H$.	Found.
Bromine	59.26	59.39

This was treated with a mixture of nitric acid and fuming sulphuric acid, precisely as in the preparation of tribromtrinitrobenzol, and yielded a product which, after removing the unattacked tribromdinitrobenzol, consisted of tribromtrinitrobenzol and tetrabromdinitrobenzol in about equal parts, thus proving that the tetrabromdinitrobenzol is not derived from an impurity, but is formed during the process.

A second experiment had for its object to determine whether the conversion of the tribromdinitrobenzol into tetrabromdinitrobenzol was due to the fuming sulphuric acid, which might well be the case, since Bässmann[4] has observed that symmętrical tribrombenzol is converted in part into pentabrombenzol when heated with fuming sulphuric acid to 100° from a week to a fortnight. We accordingly heated another quantity of the pure tribromdinitrobenzol with an excess of fuming sulphuric acid in a sealed tube to 100° for twelve hours, but no tetrabromdinitrobenzol was formed, and, as the temperature of our mixture during the manufacture of the tribromtrinitrobenzol could have been little, if at all, above 100°,

[1] Ber. d. chem. Ges. **8**, 1427.
[2] Ber. d. chem. Ges. **8**, 1426.
[3] Gazz. chim. ital. 1874, 425.
[4] Ann. Chem. (Liebig) **191**, 208.

and that process was carried on for only five hours, we are inclined to ascribe the formation of the tetrabrom compound to the nitric rather than the sulphuric acid.

In a third experiment the mixture of tribromdinitrobenzol with nitric and fuming sulphuric acids was boiled for only a quarter of an hour, instead of for the usual five hours, and the proportion of tetrabromdinitrobenzol formed was comparatively small, it would seem, therefore, that it is formed chiefly in the later part of the boiling; but it is not advantageous in preparing tribromtrinitrobenzol to diminish the length of the boiling, as the superior purity of the product does not compensate for the much smaller yield. We may add that another experiment showed that it was impossible to convert tribromtrinitrobenzol into tetrabromdinitrobenzol by boiling it with the mixture of nitric acid and fuming sulphuric acid.

Von Richter, the discoverer of tetrabromdinitrobenzol, gave the melting point 227°–228°, whereas our substance showed a constant melting point of 224°. We are of the opinion, however, that von Richter's melting point is more correct than ours, as it might well be that a small quantity of tribromtrinitrobenzol, sufficient to lower the melting point 4°, could not be removed by crystallisation, and in fact our analysis seems to indicate the presence of such an impurity; but as our object was to identify the substance rather than study its properties, we did not think it worth while to sacrifice the large amount of time and labor which would undoubtedly have been necessary to settle this point thoroughly. Von Richter also states that it is soluble in alcohol or benzol, and Bodewig[1] has published a thorough description of its crystalline form. The following properties, which we have had occasion to study, have not been published heretofore, so far as we can find. It begins to sublime at about 175°, and is soluble in methyl alcohol, ether, acetone, glacial acetic acid, or carbonic disulphide; the best solvent for it is a mixture of alcohol and benzol, in the former of which it is but sparingly soluble. It dissolves in cold sulphuric acid, but is precipitated unchanged on dilution. When heated over a free flame with sulphuric acid it is destroyed. The bromine in it is much more firmly attached to the molecule than in the tribromtrinitrobenzol, as it is not removed when the substance is boiled with alcoholic ammonia in open vessels. It is also very hard to

[1] Ztschr. Kryst. **3**, 398.

effect its complete decomposition in its analysis according to Carius.

Finally, we may remark that it is highly probable that the substance melting above 200° obtained by Wurster and Beran by heating tribromdinitrobenzol to 220° in a sealed tube with a mixture of fuming nitric and sulphuric acids was the tetrabromdinitrobenzol.

LX.—SILICOTETRAFLUORIDES OF CERTAIN BASES.[1]

By Arthur M. Comey and F. W. Smith.

Supplementary to the investigations[2] made by C. Loring Jackson and one of us on the action of fluoride of silicon on organic bases, we have further tried the action of fluoride of silicon on nitrosodimethylaniline, pyridine, cinchonine, and quinine.

Trinitrosodimethylaniline disilicotetrafluoride, $(C_8H_{10}N_2O_2)_3(SiF_4)_2$.—This compound was formed by passing fluoride of silicon through a solution of the base in benzol. A lemon-yellow precipitate was formed, which was washed thoroughly with benzol and dried at 100°. The following results were obtained from the analysis of this product:

0.1822 gram of the substance gave 0.0345 gram of silicic dioxide and 0.0936 gram of sodic fluoride.

	Calculated for $(C_8H_{10}N_2O_2)_3(SiF_4)_2$.	Found.
Silicon	8.54	8.83
Fluorine	23.09	23.25

Trinitrosodimethylaniline disilicotetrafluoride is a bright yellow amorphous powder which is decomposed by water, with separation of silicic dioxide, and decomposes completely with slight explosion when heated above 150°.

Dipyridine silicotetrafluoride, $(C_5H_5N)_2SiF_4$.—This substance was prepared by passing fluoride of silicon through a solution of pyridine in benzol, whereupon it separates out in the form of a heavy voluminous precipitate, which when washed with benzol and dried, and immediately analysed, gave the following results:

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] This Journal **10**, 165.

0.3132 gram of the substance gave 0.0925 gram of silicic dioxide and 0.2039 gram of sodic fluoride.

	Calculated for $(C_5H_5N)_2SiF_4$.	Found.
Silicon	10.77	10.81
Fluorine	29.00	29.45

Dipyridine silicotetrafluoride is a pure white amorphous powder which decomposes upon standing, giving off pyridine and forming tripyridine disilicotetrafluoride.

Tripyridine disilicotetrafluoride, $(C_5H_5N)_3(SiF_4)_2$.—This compound is formed by subliming the previous substance. Pyridine is given off and tripyridine disilicotetrafluoride sublimes, forming a crust possessing a distinct crystalline structure. It is extremely deliquescent and was not obtained in a pure state for analysis. The following results of the analysis of the slightly deliquesced substance leave no doubt as to its true constitution.

0.1743 gram of the substance gave 0.0443 gram of silicic dioxide and 0.1248 gram of sodic fluoride.

	Calculated for $(C_5H_5N)_3(SiF_4)_2$.	Found.
Silicon	12.68	11.86
Fluorine	34.14	32.16

When fluoride of silicon was passed into the ethereal solutions of *cinchonine* or *quinine*, a gummy substance separated which probably possessed a constitution similar to that of the above substances.

The constitution of these substances has been discussed at length in a previous paper[1] by C. Loring Jackson and one of us. It remains only to add that the compounds of which dianiline silicotetrafluoride is the type seem to be formed first. These are very unstable, giving up one molecule of the base with the greatest ease to form compounds corresponding to trianiline disilicotetrafluoride. This extra molecule of the base in most cases is separated by merely washing with a solvent as benzol, as in the case of aniline, toluidine, diphenylamine, chinoline, etc. In others, as dimethylamine and pyridine, the extra molecule is only given off upon standing, or by the action of heat.

Boron trifluoride gave products with organic bases which apparently possess an analogous constitution, but the substances formed were not further investigated.

[1] This Journal **10**, 165.

According to Schiff,[1] stannic tetrachloride forms an addition product with aniline, of the composition $(C_6H_7N)_4SnCl_4$. With diphenylamine, however, we obtained by the action of stannic tetrachloride a product, melting at 180°–181°, containing no tin; chlorine was present in large quantity. The investigation of the action of stannic tetrachloride on organic bases will be continued by one of us.

The above work was done in the Summer School of Chemistry at Harvard College.

ON THE ACTION OF PHOSPHORUS PENTACHLORIDE ON THE THREE ISOMERIC MONO-HYDROXY-BENZOIC ACIDS.[2]

By Richard Anschütz and George D. Moore.

After a brief account of earlier work on the subject of the action of phosphorus pentachloride on salicylic acid, the authors begin the account of their own experiments.

I. *The action of a single molecule of phosphorus pentachloride on salicylic acid: Formation of the chloride* o-$C_7H_4Cl_2PO_2$.

As raw material we employed exclusively salicylic acid, which was thoroughly dried by several days' standing over sulphuric acid in desiccators. We brought but one molecule of phosphorus pentachloride into reaction with one molecule of salicylic acid, the experience of Couper and others having shown that any excess over this amount was superfluous, and we were thus further enabled to follow the reaction step by step. We found that the reaction runs very easily of itself. After the evolution of hydrochloric acid is finished, there remains a light yellow liquid, which we at once distilled in a vacuum. We found that, as Drion and Couper had

[1] Jsb. Chem. 1863, 412.

[2] Abstract of papers which appeared in the Annalen der Chemie, Vol. **228**, page 308, Vol. **239**, pages 314 and 333, and were afterwards communicated to this Journal by the authors. For the analytical details see the original articles.

stated, only a very small amount of phosphorus oxychloride was formed. As soon as this was distilled off, the temperature rose rapidly until, under a mercury pressure of 11 mm., a clear, colorless, highly refractive liquid distilled over, constant at 168°, only a relatively small amount of a dark colored syrup remaining behind. Drion's statement that the product of the action of phosphorus pentachloride on salicylic acid is not volatile without decomposition, even under diminished pressure, is therefore a mistake. The analyses of this liquid, purified by several distillations, and finally boiling quite constant at 168° under 11 mm. pressure, gave figures in accordance with the formula $C_7H_4Cl_3PO_3$.

If to one equivalent of salicylic acid rather more than one equivalent of phosphorus pentachloride be employed, a much better yield of the chloride *o*-$C_7H_4Cl_3PO_3$ is obtained.

If the chloride *o*-$C_7H_4Cl_3PO_3$ be treated with water, it behaves differently according to the amount of water employed. If a small quantity of water be poured over it, the mixture gradually becomes warm, and finally gives a clear solution; from this solution only salicylic acid crystallises out on cooling. If, on the other hand, a large amount of water is added to the chloride, and the mixture be shaken thoroughly, cooling if necessary, until solution results, the liquid thus obtained gives no reaction for salicylic acid: it is only after several days' standing that this reaction can be observed. If, however, the solution, prepared in the cold and with a large amount of water as above described, *be boiled*, the products are salicylic, phosphoric and hydrochloric acids.

Inasmuch as the first product of an excess of water upon the chloride evidently contained phosphorus, and constituted a body which yielded salicylic acid, we attempted to isolate it by quick evaporation in a vacuum. We obtained in this manner a white, amorphous substance, free of chlorine but containing phosphorus, which melted at about 147° and was almost entirely soluble in a small amount of water. There remained undissolved in this case a few fine white needles, which the addition of ferric chloride solution at once proved to be salicylic acid.

It is evidently impossible to obtain the above-mentioned product in a state of absolute purity, owing to the readiness with which, in the presence of water, it goes over into salicylic acid. An analysis showed it to have the composition $C_7H_7PO_6$.

If the chloride *o*-$C_7H_4Cl_3PO_3$ be treated with one equivalent

of water in the shape of anhydrous oxalic acid, two chlorine atoms are replaced by one of oxygen, and a compound of the formula o-$C_7H_4ClPO_4$ results, the reaction being:

$$o\text{-}C_7H_4Cl_2PO_3 + C_2O_4H_2 = o\text{-}C_7H_4ClPO_4 + CO + CO_2 + 2HCl.$$

This substance is a white crystalline body and melts at 80°.

In order to explain the constitution of the chloride o-$C_7H_4Cl_2PO_3$ we must consider salicylic acid both as an acid and as a phenol, *i. e.* as ortho-carboxylphenol. Phosphorus pentachloride acts very readily upon the carboxyl group, forming the chlorcarbonyl group COCl. The by-products are phosphorus oxychloride and hydrochloric acid. The former reacts upon phenol, forming phenyl-ortho phosphoric acid dichloride, as Jacobsen[1] has recently shown. Salicylic acid contains both the carboxyl and hydroxyl groups: the first is attacked by the phosphorus pentachloride and gives the chlorcarbonyl group, phosphorus oxychloride and hydrochloric acid. The phosphorus oxychloride then attacks the phenol-hydroxyl and forms the group $OPOCl_2$ plus hydrochloric acid. The final product is therefore $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases}$, the reactions being:

$$C_6H_4\begin{cases}(1)\ COOH\\(2)\ OH\end{cases} + PCl_5 = C_6H_4\begin{cases}(1)\ COCl\\(2)\ OH\end{cases} + POCl_3 + HCl;$$

$$C_6H_4\begin{cases}(1)\ COCl\\(2)\ OH\end{cases} + POCl_3 = C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases} + HCl.$$

The product so obtained is Couper's "trichlorophosphat de salicyl." From the reactions it is evident why only one equivalent of phosphorus pentachloride enters into the reaction, why but little phosphorus oxychloride is formed, and why, finally, the product, if treated with a small amount of water, forms hydrochloric and salicylic acids; with a larger quantity, on the other hand, a soluble compound, in which the salicylic acid residue doubtless plays a part similar to that of the phenol residue in the monophenyl-ortho-phosphoric acid. According to its constitution this

[1] Ber. d. chem. Ges. **8**, 1521.

[2] Later investigations, the preliminary results of which have already been published by Emery and one of us in a paper entitled "Über die Einwirkung von Phosphortrichlorid auf Salicylsäure" (Ann. der Chemie **233**, 301), after the completion of our research, show that in regard to the constitutional formula of the chloride o-$C_7H_4Cl_2PO_3$ which we have written $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases}$, the formula $C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl_3$ is also worthy of consideration. For the present, however, we prefer the first formula, suspending all judgment for or against the second until the research in connection therewith has been completed.

"trichlorophosphat de salicyl" may be designated as *ortho-chlorcarbonyl-phenyl-ortho-phosphoric dichloride.*

Two determinations of the specific gravity gave $d_4^{20} = 1.55513$ and 1.55215; mean = 1.55364.

The action of a second molecule of phosphorus pentachloride on the chloride o-$C_7H_4Cl_2PO_2$: *Formation of the chloride* o-$C_7H_4ClPO_2$.

If equal molecules of the chloride o-$C_7H_4Cl_2PO_2$ and phosphorus pentachloride be heated together in sealed tubes at 165°–170° until everything is dissolved, it is at once evident, from the increase in the volume of the liquid, that a reaction has taken place. On rectifying the contents of the tubes under diminished pressure, a large quantity of phosphorus oxychloride is first obtained, more or less phosphorus pentachloride subliming over at the same time. Between 165° and 170° a small amount of unchanged chloride, o-$C_7H_4Cl_2PO_2$, comes over; the principal product, however, boils at 176°–179°, the pressure being 11–12 mm. For the analyses, a portion boiling constant at 178° under 11–12 mm. pressure was employed.

The results of the analyses show that the compound has the composition o-$C_7H_4ClPO_2$. It is formed thus:

$$o\text{-}C_7H_4Cl_2PO_2 + PCl_5 = o\text{-}C_7H_4ClPO_2 + POCl_3.$$

As in the case of the chloride o-$C_7H_4Cl_2PO_2$, a much better yield of this product is obtained when an excess of phosphorus pentachloride is employed.

The action of a third molecule of phosphorus pentachloride on the chloride: Formation of ortho-chlorbenzotrichloride.

Pure $C_7H_4Cl_2PO_2$ was heated with rather more than one equivalent of phosphorus pentachloride in closed tubes at about 180°. After several days' heating all the pentachloride was dissolved and the contents of the tube consisted of a clear yellowish liquid. No pressure was manifested as the tubes were opened. The raw product was rectified under diminished pressure, and the first distillate consisted of a large quantity of phosphorus oxychloride, together with more or less pentachloride. The greater part of the remainder boiled between 135° and 150°, under 13–14 mm. pressure; the last portion, however, probably unchanged $C_7H_4Cl_2PO_2$,

between 175° and 180°. On being again rectified, this fraction came over between 128° and 131° as a clear colorless liquid which, in a cooling mixture, solidified to a white crystalline mass. The analyses showed that it is ortho-chlorbenzo-trichloride, $C_7H_4Cl_4$ $\left(=C_6H_4\begin{cases}(1)\,CCl_3\\(2)\,Cl\end{cases}\right)$.

The following reactions express, step by step, the action of phosphorpentachloride on salicylic acid:

$$C_6H_4\begin{cases}(1)\,COOH\\(2)\,OH\end{cases}+PCl_5=o\text{-}C_7H_4Cl_3PO_2+2HCl;$$

$$o\text{-}C_7H_4Cl_3PO_2+PCl_5=o\text{-}C_7H_4Cl_5PO_2+POCl_3;$$

$$o\text{-}C_7H_4Cl_5PO_2+PCl_5=C_6H_4\begin{cases}(1)\,CCl_3\\(2)\,Cl\end{cases}+2POCl_3.$$

Starting from the two different constitutional formulas of the chloride o-$C_7H_4Cl_3PO_2$, we perceive that not only the chloride o-$C_7H_4ClPO_4$, but also the chloride o-$C_7H_4Cl_5PO_2$, may have one of two different constitutional formulas. All these formulas are given in the following table:

o-$C_7H_4ClPO_4$	$C_6H_4\begin{cases}(1)\,COCl\\(2)\,OPO_2\end{cases}$	$C_6H_4\begin{cases}(1)\,COO\\(2)\,O\end{cases}>POCl$
o-$C_7H_4Cl_3PO_2$	$C_6H_4\begin{cases}(1)\,COCl\\(2)\,OPOCl_2\end{cases}$	$C_6H_4\begin{cases}(1)\,COO\\(2)\,O\end{cases}>PCl_3$
o-$C_7H_4Cl_5PO_2$	$C_6H_4\begin{cases}(1)\,CCl_3\\(2)\,OPOCl_2\end{cases}$	$C_6H_4\begin{cases}(1)\,COCl\\(2)\,OPCl_4\end{cases}$

Since the chloride o-$C_7H_4Cl_5PO_2$ is easily converted by water into the acid o-$C_7H_4PO_2(OH)_2$, it would follow from the formula $C_6H_4\begin{cases}(1)\,CCl_3\\(2)\,OPOCl_2\end{cases}$ that the ortho-oxybenzo-trichloride (a compound thus far unknown) is either incapable of existence in the presence of water, or under these conditions is easily converted into salicylic acid. The formula $C_6H_4\begin{cases}(1)\,COCl\\(2)\,OPCl_4\end{cases}$ has, thus far, its sole analogue in the compound $C_6H_5OPCl_4$.[1] The behavior of the chloride o-$C_7H_4Cl_5PO_2$ could be explained with the help of it, as well as by using the first of the above mentioned formulas.

We hope that we shall be able to explain the constitution of the chloride o-$C_7H_4Cl_5PO_2$ by the help of synthetical reactions.

[1] Ann. d. Chemie **239**, 312.

Decomposition of the chloride o-$C_7H_4Cl_3PO_3$ *by distillation under ordinary pressure.*

If the chloride be distilled rapidly, it conducts itself in the same way as "trichlorophosphat de salicyl," as described by Couper. At a temperature somewhat over 300°, hydrochloric acid is given off, and a liquid distills over, in which, after several days' standing in a sealed tube, large transparent crystals are deposited. These crystals melted at 80°, and in general form and appearance were identical with the product already described which was obtained by the action of anhydrous oxalic acid on the chloride o-$C_7H_4Cl_3PO_3$.

A series of elaborate experiments was now undertaken to determine the character of the decomposition of the chloride when it is distilled slowly under ordinary pressure. The products obtained were phosphorus oxychloride, o-chlor-benzoyl chloride, o-chlor-benzo-trichloride, and the compound o-$C_7H_4ClPO_4$.

It has been shown that the chloride o-$C_7H_4Cl_3PO_3$ gives, with anhydrous oxalic acid, the chloride o-$C_7H_4ClPO_4$, two chlorine atoms being replaced by one of oxygen. It is highly probable that both these chlorine atoms are attached to phosphorus, and under this assumption, the rest, PCl_3, behaves toward anhydrous oxalic acid in a manner quite similar to phosphorpentachloride:

$$Cl_3PCl_2 + (COOH)_2 = Cl_3PO + CO_2 + CO + 2HCl;$$

$$o\text{-}C_7H_4ClO_3PCl_2 + (COOH)_2 = o\text{-}C_7H_4ClO_3PO + CO_2 + CO + 2HCl.$$

If we consider, further, that by the action of phosphorus pentachloride, the chloride o-$C_7H_4Cl_3PO_3$ is converted first, at a temperature of 160°–165°, into the chloride o-$C_7H_4Cl_5PO_2$, and this by still further action of phosphorus pentachloride at 180° into ortho-chlor-benzo-trichloride, phosphorus oxychloride being in each case the by-product, according to the reactions:

$$o\text{-}C_7H_4Cl_3PO_3 + PCl_5 = o\text{-}C_7H_4Cl_5PO_2 + POCl_3,$$

$$o\text{-}C_7H_4Cl_5PO_2 + PCl_5 = C_6H_4\begin{cases}(1)\ CCl_3\\(2)\ Cl\end{cases} + 2POCl_3,$$

we may readily assume that the two chlorine atoms in the chloride o-$C_7H_4Cl_3PO_3$ which behave toward anhydrous oxalic acid in the same manner as the two chlorine atoms of phosphorus pentachloride, can play a similar part in other reactions, *e. g.* by heating with another molecule o-$C_7H_4Cl_3PO_3$ at high temperature. This assumption seems all the more probable from the

fact that we find a large amount of the chloride o-$C_7H_4ClPO_4$ among the decomposition products obtained by slowly heating the chloride o-$C_7H_4Cl_3PO_3$ under ordinary pressure. The chloride o-$C_7H_4ClPO_4$ takes the place of the phosphorus oxychloride formed in the phosphorus pentachloride reaction; it is formed by the replacement of two chlorine atoms of the chloride o-$C_7H_4Cl_3PO_3$ by an oxygen atom, and these chlorine atoms served for the production of the ortho-chlor-benzoyl and ortho-chlor-benzo-trichlorides, as well as of the chloride o-$C_7H_4Cl_3PO_2$ from which, by the splitting off of phosphorus oxychloride, the ortho-chlor-benzo-trichloride is formed.

The following reactions serve to explain the decomposition process which takes place when the chloride o-$C_7H_4Cl_3PO_3$ is slowly heated under ordinary pressure:

I. $o\text{-}C_7H_4Cl_3PO_3 + o\text{-}C_7H_4Cl_3PO_3 =$
$$o\text{-}C_7H_4ClPO_4 + C_6H_4\begin{cases}(1)\ COCl\\(2)\ Cl\end{cases} + POCl_3;$$

II. $o\text{-}C_7H_4Cl_3PO_3 + o\text{-}C_7H_4Cl_3PO_3 =$
$$o\text{-}C_7H_4ClPO_4 + o\text{-}C_7H_4Cl_3PO_2;$$

III. $o\text{-}C_7H_4Cl_3PO_2 + o\text{-}C_7H_4Cl_3PO_3 =$
$$o\text{-}C_7H_4ClPO_4 + C_6H_4\begin{cases}(1)\ CCl_3\\(2)\ Cl\end{cases} + POCl_3.$$

From this general formulation we see that the interpretation of the decomposition of the chloride o-$C_7H_4Cl_3PO_3$ is independent of the constitutional formulas of the phosphorus derivatives of salicylic acid. A much better idea of the course of the reactions is obtained by the use of graphic formulas. Thus, assuming the constitution of the first product of the action of phosphorus pentachloride on salicylic acid to be $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases}$, we may write the last three equations as follows:

I. $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases} + C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases} =$
$$C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPO_2\end{cases} + C_6H_4\begin{cases}(1)\ COCl\\(2)\ Cl\end{cases} + POCl_3;$$

II. $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases} + C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases} =$
$$C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPO_2\end{cases} + \begin{matrix}C_6H_4\begin{cases}(1)\ CCl_3\\(2)\ OPOCl_2\end{cases}\\ \text{or}\\ C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPCl_4\end{cases}\end{matrix};$$

III. $C_6H_4\begin{cases}(1)\ CCl_3\\(2)\ OPOCl_2\end{cases}$ or $+C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases}=$

$C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPCl_4\end{cases}$

$$C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPO_2\end{cases}+C_6H_4\begin{cases}(1)\ CCl_3\\(2)\ Cl\end{cases}+POCl_3.$$

Assuming now that the constitution of the first chloride o-$C_7H_4Cl_3PO_3$ is $C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl_3$, we may write:

I. $$C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl_3+C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl_3=$$
$$C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>POCl+C_6H_4\begin{cases}(1)COCl\\(2)Cl\end{cases}+POCl_3;$$

II. $$C_6H_4\begin{cases}(1)COO\\(2)O\end{cases}>PCl_3+C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl_3=$$
$$C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>POCl+C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPCl_4\end{cases};$$

III. $$C_6H_4\begin{cases}(1)COO\\(2)O\end{cases}>PCl_3+C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPCl_4\end{cases}=$$
$$C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>POCl+C_6H_4\begin{cases}(1)\ CCl_3\\(2)\ Cl\end{cases}+POCl_3.$$

As soon as experiments (which have already been begun) have established the constitution of the three chlorides o-$C_7H_4ClPO_4$, o-$C_7H_4Cl_3PO_3$, and o-$C_7H_4Cl_3PO_2$, we shall be in a position to determine which of the above series of reactions is the correct one.

By the results above described, concerning the action of phosphorus pentachloride on salicylic acid, we have obtained, for the first time, a correct idea of the action of phosphorus pentachloride upon an aromatic mono-hydroxy-mono-carboxy-acid. For the purpose of completing the generalisation of the reaction, we have extended it to the two isomers of salicylic acid—the meta- and para-hydroxy-benzoic acids.

The Action of Phosphorus Pentachloride upon Meta-hydroxy-benzoic Acid.

Action of one molecule of phosphorus pentachloride on meta-hydroxy-benzoic acid. Formation of the chloride,

$$C_6H_4\begin{cases}(1)\ COCl\\(3)\ OPOCl_2\end{cases}.$$

Perfectly pure, dry meta-hydroxy-benzoic acid was mixed in a

flask with a little more than one equivalent of phosphorus pentachloride. Both substances dissolved slowly with evolution of hydrochloric acid, and constituted finally a clear yellow liquid. This, after warming a few minutes at 100° to expel the last traces of hydrochloric acid, was immediately rectified in a vacuum. At first a small quantity of phosphorus oxychloride mixed with pentachloride came over, then the temperature rose rapidly, and between 160° and 180°, under 11-12 mm. pressure, a colorless liquid distilled over. Upon being again distilled, this product boiled between 168° and 170° under 11 to 12 mm. pressure. The analytical results led to the formula $C_7H_4Cl_2PO_3\left(=C_6H_4\begin{cases}(1)\ COCl\\(3)\ OPOCl_2\end{cases}\right)$.

The specific gravity, determined by means of a Sprengel's U-shaped pyknometer, is $d^{\frac{20}{4}} = 1.54844$.

The chloride, *m*-$C_7H_4Cl_2PO_3$, thus formed is therefore isomeric with the compound obtained by the action of phosphorus pentachloride on salicylic acid. While, however, for the latter, both of the formulas $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases}$ and $C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl_3$ are worthy of consideration, in the case of the meta-chloride the second formula is highly improbable, as in the case of meta-compounds in general, experience has shown that the chains in the meta-position do not condense to form closed rings. We prefer, therefore, for this first product of the action of phosphorus pentachloride on meta-hydroxy-benzoic acid the formula $C_6H_4\begin{cases}(1)\ COCl\\(3)\ OPOCl_2\end{cases}$.

The reaction would then be as follows:

$$C_6H_4\begin{cases}(1)\ COOH\\(3)\ OH\end{cases}+PCl_5=C_6H_4\begin{cases}(1)\ COCl\\(3)\ OH\end{cases}+POCl_3+HCl;$$

$$C_6H_4\begin{cases}(1)\ COCl\\(3)\ OH\end{cases}+POCl_3=C_6H_4\begin{cases}(1)\ COCl\\(3)\ OPOCl_2\end{cases}+HCl.$$

Treated with water, the chloride dissolved slowly under evolution of heat and hydrochloric acid. From this solution crystallised, on cooling, fine white leaflets of a substance extremely soluble in water, alcohol and ether. On recrystallising from alcohol, this product melted at 200°–201°, and the analyses led to the formula

$$C_7H_7PO_6\left(=C_6H_4\begin{cases}(1)\ COOH\\(3)\ OPO_3H_2\end{cases}\right).$$

From its formation, and from the results obtained by the an-

alyses, we may designate this body as meta-carboxyl-phenyl-orthophosphoric acid. Its formation is explained by the reaction:

$$C_6H_4\begin{cases}(1)\ COCl\\(3)\ OPOCl_2\end{cases}+3H_2O=C_6H_4\begin{cases}(1)\ COOH\\(3)\ OPO(OH)_2\end{cases}+3HCl.$$

Decomposition of the meta-chlorcarbonyl-phenyl-orthophosphoric dichloride by distillation under ordinary pressure.

About thirty grams of pure chloride were heated on a graphite bath. The temperature rose slowly, until between 315° and 322° a colorless mobile liquid, smelling strongly of phosphorus oxychloride, distilled over, the residue in the retort forming a thick black substance, which when warm was liquid, but upon cooling became quite solid.

The distillate was immediately rectified under ordinary pressure. The larger part thereof boiled between 108° and 112°, and from this, as well as from its other properties, was easily recognised as phosphorus oxychloride. As soon as this fraction had distilled over, the temperature rose rapidly, and the remaining substance came over between 300° and 310°, no residue of any consequence being left. This second fraction was then rectified under diminished pressure, and boiled between 165° and 175° under a pressure of 13-14 mm. Decomposed with water, it gave hydrochloric acid and a precipitate of white leaflets melting between 200° and 201°, which, on analysis, proved to be meta-carboxyl-phenyl-orthophosphoric acid.

Although the formation of phosphorus oxychloride during the distillation under ordinary pressure would seem to indicate that a decomposition of the original chloride had taken place, we were nevertheless unable to isolate from the decomposition product any meta-chlor-benzoyl chloride. The boiling point of the second fraction, and its behavior with water, proved conclusively that it consisted essentially of unchanged chloride. From the residue, which it was not possible to distill further, we recovered, by means of water or alkali, only meta-hydroxy-benzoic acid.

The most important result of these experiments in decomposing the meta-chloride is evidently this: the phenol-oxygen atom which is in the *meta*-position is by no means so easily replaced by chlorine as the phenol-oxygen atom which occupies the corresponding position in the *ortho*-compound.

The action of a second molecule of phosphorus pentachloride on meta-chlor-carbonyl-phenyl-orthophosphoric dichloride. Formation of the chloride m-$C_7H_4Cl_5PO_2$.

The reaction was carried out in a manner exactly analogous to that described under the corresponding ortho-compound, rather more than equal molecules of each substance being employed, in order to insure a better yield of product. After heating the tubes for about thirty hours, the phosphorus pentachloride dissolved completely, and the product consisted of a clear yellow liquid. On opening the tubes, no pressure of any consequence was manifested. On rectifying under diminished pressure, we obtained as the first fraction a large amount of phosphorus oxychloride mixed with more or less pentachloride. A small amount of unchanged chloride came over between 160° and 175° under 11 mm., but the chief product boiled between 176° and 179°, the pressure remaining the same. The residue consisted of a relatively small amount of a yellowish syrup which could not be distilled further.

Analyses of a portion boiling at 178° under 11 mm. pressure gave results in accordance with the formula $C_7H_4Cl_5PO_2$, and the compound is evidently analogous to that obtained under similar conditions from salicylic acid. For this latter we have already suggested two formulas, $C_6H_4\begin{cases}(1)\ CCl_3\\(2)\ OPOCl_2\end{cases}$ and $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPCl_4\end{cases}$.

Under the assumption that ortho-oxybenzo-trichloride (which is as yet unknown) is easily converted by water into salicylic acid, we may explain the behavior of the chloride *o-*$C_7H_4Cl_5PO_2$ with water on the basis of the first constitutional formula. Although this assumption in the case of the ortho-oxybenzo-trichloride seems, to a certain degree, justifiable, there is, nevertheless, no reason for the supposition that the meta-oxybenzo-trichloride (also unknown) acts in the same manner. Consequently we expected that the chloride *m-*$C_7H_4Cl_5PO_2$, by treatment with water, would go over into the acid $C_6H_4\begin{cases}(1)\ CCl_3\\(3)\ OPO(OH)_2\end{cases}$ if its constitutional formula was $C_6H_4\begin{cases}(1)\ CCl_3\\(3)\ OPOCl_2\end{cases}$. As a matter of fact, however, on being brought together with water, all the chlorine was eliminated, and, with a violent effervescence of hydrochloric acid, a crystalline compound—the above-described *m*-carboxyl-phenyl-orthophosphoric acid—was formed:

$$m\text{-}C_7H_4Cl_5PO_2 + 4H_2O = C_6H_4\begin{cases}(1)\ COOH\\(3)\ OPO(OH)_2\end{cases} + 5HCl.$$

After being once recrystallised from water, this compound melted at 200°–201°.

This direct formation of *m*-carboxy-phenyl-orthophosphoric acid by the action of cold water on the chloride $m\text{-}C_7H_4Cl_5PO_2$, we consider a valuable argument for the formula $C_6H_4\begin{cases}(1)\ COCl\\(3)\ OPCl_4\end{cases}$, for which we hope to be able to furnish later direct experimental proof.

The action of a third molecule of phosphorus pentachloride upon the chloride $m\text{-}C_7H_4Cl_5PO_2$. *Formation of meta-chlor-benzo-trichloride.*

The reaction was carried out in a manner quite analogous to that employed in the case of the corresponding ortho-compound. A slight excess of phosphorus pentachloride was used, and after three days' heating at 170°–180° all had dissolved, and the contents of the tubes consisted of a clear yellowish liquid. No pressure of any consequence was observed when the tubes were opened. Rectified under diminished pressure, the following products were obtained. First, a large quantity of phosphorus oxychloride, mixed with more or less pentachloride, came over, then the greater part of what remained in the retort between 123° and 137° under 14–15 mm. pressure. A relatively small portion, undoubtedly unchanged chloride and boiling at 175°–180°, formed the last fraction. No residue worth mentioning remained in the retort.

The second fraction was immediately rectified under ordinary pressure, and showed the boiling point 247° to 250°, no residue remaining. An analysis showed that it was almost pure meta-chlorbenzo-trichloride.

From this we may reasonably conclude that phosphorus pentachloride reacts upon meta-trichlor-methyl-phenyl-ortho-phosphoric dichloride exactly as upon the corresponding ortho-compound, the equation being

$$C_6H_4\begin{cases}(1)\ CCl_3\\(3)\ OPOCl_2\end{cases} + PCl_5 = C_6H_4\begin{cases}(1)\ CCl_3\\(3)\ Cl\end{cases} + 2POCl_3.$$

The Action of Phosphorus Pentachloride upon Para-hydroxybenzoic Acid.

Action of the first molecule, forming the chloride

$$C_6H_4\begin{cases}(1)\ COCl\\(4)\ OPOCl_2\end{cases}.$$

Para-hydroxybenzoic acid crystallises with one molecule of water, which must be removed by heating at 100° before the phosphorus pentachloride can be added. The dry acid and phosphorus pentachloride on being brought together enter into reaction much more violently than either salicylic or meta-hydroxybenzoic acid. Hydrochloric acid is given off rapidly, and the temperature rises so high that in cases where more than 10 or 15 grams of acid are employed, it is advisable to cool the mixture. The raw product consists of a clear yellowish liquid which, on being distilled under diminished pressure, yields as the first fraction phosphorus oxychloride and pentachloride. The temperature then rises rapidly to about 165°, and the greater part of the remaining substance distills over between 165° and 170° under 12 mm. pressure. The residue, a relatively small portion only of the original contents of the retort, is a thick dark syrup from which, by boiling with water, para-oxybenzoic acid is easily recovered.

The analyses led to the formula

$$C_7H_4Cl_2PO_2\left(=C_6H_4\begin{cases}(1)\ COCl\\(4)\ OPOCl_2\end{cases}\right).$$

The specific gravity of the compound is $d^{20}_{4} = 1.54219$.

According to its constitution we may designate it as *para-chlorcarbonyl-phenyl-orthophosphoric dichloride*, the reactions by which it is formed being:

$$C_6H_4\begin{cases}(1)\ COOH\\(4)\ OH\end{cases} + PCl_5 = C_6H_4\begin{cases}(1)\ COCl\\(4)\ OH\end{cases} + POCl_3 + HCl;$$

$$C_6H_4\begin{cases}(1)\ COCl\\(4)\ OH\end{cases} + POCl_3 = C_6H_4\begin{cases}(1)\ COCl\\(4)\ OPOCl_2\end{cases} + HCl.$$

As in the case of salicylic and meta-hydroxybenzoic acids, a much better yield of the chloride is obtained by using an excess of phosphorus pentachloride.

This chloride, if treated with water, behaves quite like the meta-compound. Hydrochloric acid is given off, and the residual liquid deposits, on cooling, a heavy precipitate of white leaflets melting at 200° and very easily soluble in water, alcohol and ether.

An analysis proved it to be *para-carboxyl-phenyl-orthophosphoric acid*, $C_6H_4\begin{cases}(1)\ COOH\\(4)\ OPO(OH)_2\end{cases}$. It is formed according to the following reaction:

$$C_6H_4\begin{cases}(1)\ COCl\\(4)\ OPOCl_2\end{cases}+3H_2O=C_6H_4\begin{cases}(1)\ COOH\\(4)\ OPO(OH)_2\end{cases}+3HCl.$$

As in the case of the corresponding meta-compound, the para-carboxyl-phenyl-orthophosphoric acid is very stable. Neither compound gives up its phosphoric acid even by boiling with potash. The para-compound, however, may be broken up into para-hydroxybenzoic acid and phosphoric acid by heating with water for several hours at 150°–160° in a sealed tube.

Decomposition of the chloride $C_6H_4\begin{cases}(1)\ COCl\\(4)\ OPOCl_2\end{cases}$ *by slow distillation under ordinary pressure.*—20 grams of pure chloride were heated on a graphite bath just as in the case of the meta-chloride. The temperature, measured by a thermometer dipping below the surface of the liquid in the flask, rose rapidly, and between 325° and 330° a clear colorless fluid began to distill over. Toward the end of the operation the residue in the boiling-flask suddenly decomposed, leaving a mass of light puffy charcoal which completely filled the apparatus.

The distillate was rectified under diminished pressure. The first fraction consisted of a small quantity of phosphor-oxychloride, the second of a few drops of a liquid boiling between 125° and 129° under 13–14 mm. pressure. The principal part came over in the third fraction, evidently unchanged chloride, boiling between 175° and 177° under 13–14 mm. pressure. The third fraction gave, moreover, with water, para-carboxyl-phenyl-orthophosphoric acid, melting point 200°.

The second fraction, boiling point 125°–129° under 13–14 mm. pressure, was analysed and found to be almost pure para-chlorbenzoyl chloride.

The action of a second molecule of phosphorus pentachloride on the chloride $C_6H_4\begin{cases}(1)\ COCl\\(4)\ OPOCl_2\end{cases}$.—Pure chloride was heated with rather more than one equivalent of phosphorus pentachloride in a sealed tube, at first for one day at 150°. As the phosphorus pentachloride did not dissolve under these conditions, the tempera-

ture was raised on the following day to 160°, and as this did not suffice, finally on the third day to 170°–180°. At this last temperature the phosphorus pentachloride slowly dissolved, giving a clear yellow product. The first product of the rectification of this, under diminished pressure, was phosphorus oxychloride mixed with pentachloride. Under 14 mm. pressure the second fraction came over between 117° and 129°, the third between 134° and 165°, and the last between 170° and 177°. This last portion, which consisted of but a few drops, was unchanged para-chlorcarbonyl-phenyl-orthophosphoric dichloride. On being again rectified under diminished pressure (13–14 mm.), the greater part of the second fraction came over between 108° and 112°. This gave by subsequent distillation under the same pressure, two portions, the first boiling at 108°–110°, the second at 110°–112°. Both portions were analysed, and found to be, in all probability, para-chlorbenzoyl chloride, rendered slightly impure by the presence of traces of para-chlorbenzo-trichloride. From our experience in obtaining the ortho-chlorbenzoyl chloride in the pure state we concluded that it would not be worth while to attempt to isolate the para-chlorbenzoyl chloride from the accompanying para-chlor-benzo-trichloride. Moreover, all doubts as to the nature of the substance were removed on treating it with water. We obtained with ease para-chlorbenzoic acid, melting at 236°–237°, while a very small portion, smelling quite like benzo-trichloride, was not attacked.

The third fraction, bpt. under 14 mm. 134°–165°, on being again distilled under the same pressure, showed the boiling point 125°–137°. The amount of the distillate was very small, but we succeeded in making an analysis of it and thus proving it to be nearly pure para-chlorbenzo-trichloride.

From what has been shown above it is evident that the reaction of phosphorus pentachloride upon the chloride $C_6H_4\begin{cases}(1)\ COCl\\(4)\ OPOCl_2\end{cases}$ is not the same as in the case of the corresponding ortho- and meta-compounds. Upon both these last mentioned substances the first molecule reacts in such a manner that the oxygen of the group COCl is replaced by two chlorine atoms, the phenol-oxygen not being attacked. It is only by the action of a second molecule of phosphorus pentachloride that this phenol-oxygen atom is replaced by chlorine. In the case of the para-chloride, para-chlor-

benzoyl chloride is the first product, and the small amount of para-chlorbenzo-trichloride which is formed probably results from the action of phosphorus pentachloride upon it:

$$C_6H_4\begin{cases}(1)\,COCl\\(4)\,OPOCl_2\end{cases}+PCl_5=C_6H_4\begin{cases}(1)COCl\\(4)Cl\end{cases}+2POCl_3;$$

$$C_6H_4\begin{cases}(1)\,COCl\\(4)\,Cl\end{cases}+PCl_5=C_6H_4\begin{cases}(1)\,CCl_3\\(4)\,Cl\end{cases}+POCl_3.$$

In the course of the foregoing we have referred several times on the one hand to the similarity, on the other to the characteristic differences which the three isomeric mono-hydroxybenzoic acids exhibit when brought into reaction with phosphorus pentachloride. Deeming it superfluous to repeat these remarks here, we would say, in conclusion, that investigations have already been undertaken in this laboratory with a view of extending this reaction to other suitable hydroxy acids of the fatty series.

BONN, *April*, 1887.

THE ATOMIC WEIGHT OF ZINC AS DETERMINED BY THE COMPOSITION OF THE OXIDE.

BY H. N. MORSE AND W. M. BURTON.

About five years ago one of us, with Dr. E. H. Keiser, began a series of experiments upon the preparation of pure zinc, the object in view being a redetermination of the atomic weight of that element with the metal as a starting point. Other methods of preparation having proved more or less unsatisfactory, we determined to attempt the fractional distillation of the metal in a vacuum. We were not then aware of the work of A. Schuller[1] or of E. Demarçay[2] upon the distillation of substances in a vacuum. Having found by preliminary experiments made with the ordinary commercial zinc that the method was likely to prove very effective for the separation of the metal from the impurities which are usually associated with it, especially lead, we provided ourselves with a supply of the material which Dr. Schuchardt, of Goerlitz, designated in his catalogue of chemicals as "Zincum met. absolut. chem. pur. (für

[1] Jahresb. 1884, 1550. [2] Jahresb. 1882, 161.

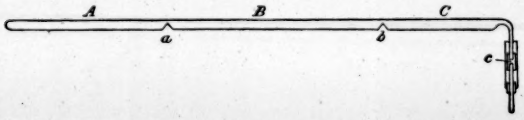
forensische Zwecke)." This was found to contain a small amount of lead and a trace of cadmium, but no other impurities. From it the pure zinc employed in our determinations has been prepared. After Dr. Keiser's removal to Bryn Mawr, the work was continued with the assistance of Dr. C. Piggot, who distilled the metal, analysed the various fractions, and also made some preliminary practice determinations of the atomic weight. The authors of this paper are much indebted to both of these gentlemen, since the experience gained while they were associated with the work, and the suggestions offered by them, have enabled us to quickly bring the method into its present simple and satisfactory form for the final determinations.

The method adopted consists in the conversion of the zinc into nitrate, the evaporation of the excess of nitric acid, and the partial decomposition of the nitrate in a hot-air bath, and, finally, the ignition of the oxide to constant weight in a muffle. The simplicity and directness of the method are strong points in its favor, and we believe we have demonstrated beyond a reasonable doubt that the objections to it offered by Marignac[1] are founded on misapprehensions.

I.—*The Preparation of Pure Zinc.*

The distillation of the zinc was effected in hard glass tubes of the size of those ordinarily employed in the combustion of carbon compounds. Fig. 1 represents their form when ready

FIG. 1.



for distillation. A tube about 650 mm. in length was fused together at one end, and from 150 to 170 grams of zinc introduced. At two points, *a* and *b*, the glass was softened in the flame of the blast lamp, and depressed by means of a red-hot file, thus dividing the tube into three compartments which we designate as *A*, *B* and *C*. The open end of the tube was then drawn out and turned

[1] Archives des Sciences Phys. et Nat. (3) **10**, 194.

down in the manner indicated. At *c* it was connected with a Sprengel air pump having a manometer attached. The attachment of the tube to the pump was made by means of rubber tubing firmly tied with waxed shoemaker's thread, and surrounded by mercury. The outside of the rubber connecting tube was washed with a solution of mercuric chloride in order to bring about a closer adhesion of the mercury. The use of glycerin joints was found to be impracticable because of the action of the vapor of zinc upon that of glycerin, by which the oxide of zinc was formed, and volatile substances were liberated whose presence rendered a high degree of exhaustion impossible.

The tube having been thoroughly exhausted was then heated in a combustion furnace throughout nearly its whole length, but most strongly in the compartment *A* containing the zinc, and least strongly in the compartment *C*. When raised to its fusing point the zinc begins to distill quite rapidly from *A* into *B*, and more slowly from *B* into *C*. The vapors from *A* condensed in *B* in the form of globules upon the glass, which when they had attained sufficient size ran down upon the floor of the tube, giving when cooled a thick bar of the metal having the form of the lower half of the tube. Those globules which were left upon the upper portion of the tube when the heat was turned off solidified into beautiful but apparently very complicated crystals. When the metal in *A* had been reduced to about one fourth of the quantity originally taken, and about one tenth of the whole had distilled into *C*, the distillation was suspended. The tube usually cracked on cooling, but not until the temperature had fallen so low that there was little danger of oxidation of the zinc resulting from the admission of air. The portion remaining in *A* and that which had collected in *C* were rejected. The portion collected in *B* was four times redistilled in the manner described. The material deposited in *B* during the fifth distillation was employed for the determination of the atomic weight. It was carefully analysed, but we were unable to find in it any impurity whatever. It was also spectroscopically examined by Mr. J. S. Ames, Fellow in Physics in this university. The following is a copy of his written report:

"I have examined spectroscopically three specimens of the zinc prepared by distillation in a vacuum. The apparatus used was Prof. Rowland's induction coil, driven by a Siemens alternating dynamo, and his 20-foot concave grating spectroscope. Photo-

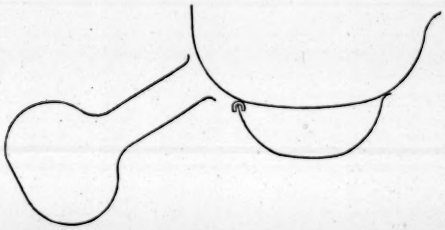
graphs were taken in the ultra violet from w. l. 4000 to w. l. 2000, with wide slit and unusually long exposures. In this region are many of the strongest lines of such metals as lead, cadmium, tin and indium ; and in a specimen of so called C. P. zinc several lines belonging to each of these metals were found on the negatives. With the zinc prepared by distillation in a vacuum, however, not a trace of any of the above impurities could be found."

The rejected portions in *A* and *C* were also analysed, but we were not able to find any impurities in them, except after the first distillation, when the contents of *A* were found to contain a small amount of lead, and those of *C* a trace of cadmium.

II.—*The Preparation of Pure Nitric Acid.*

It was found impossible by distilling from a platinum retort to prepare an acid which on evaporation would not leave a residue. The distillate contained in every case a small quantity of gold which the acid had extracted from the solder used in joining the tube to the body of the retort. We therefore made use of the following simple arrangement, Fig. 2. Two platinum dishes, one

FIG. 2.



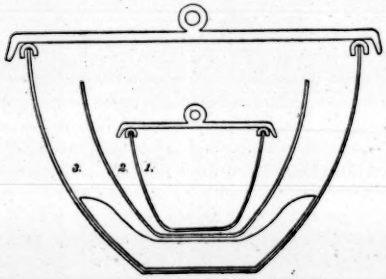
100 mm., the other 70 mm. wide, were arranged as shown in the figure, the two being kept apart by hooks of thick platinum wire hung over the edge of the lower one. The upper one was cooled by putting into it pieces of ice. The acid, having first been treated with nitrate of silver, was then slowly distilled from a small flask so placed that the vapors issuing from it would strike against and condense upon the cold surface of the upper dish. The acid thus obtained left no residue on evaporation. It was preserved by

placing the smaller dish in which it was collected under a bell jar. To transfer it from the dish to the crucible in which the zinc was to be dissolved, a platinum spoon was used.

III.—*The Arrangement of Crucibles.*

Fig. 3 exhibits the arrangement of porcelain crucibles employed for the conversion of the metal into oxide. 1 is a small crucible

FIG. 3.



(No. oo) with lid, in which the zinc is treated with nitric acid, and the nitrate converted into oxide. The crucible and its lid are separated by means of hooks of platinum wire hung over the edge. This is necessary, in order that the vapors of nitric acid and of the oxides of nitrogen may freely escape, and that there may be free diffusion between the inside and the outside. As the temperature to which the oxide is heated in the muffle is very high—as high, at least, as that required for the fusion of steel, and far above that at which the glaze upon porcelain ware begins to soften, it is necessary to remove the glaze from the under side of the crucible lid; otherwise the lid would be found to be firmly stuck to the platinum hooks which separate it from the crucible. This removal is easily effected by means of hydrofluoric acid. 2 is a larger crucible (No. II) without lid, from the outside of which the glaze has also been removed to prevent sticking. 1 and 2 are weighed together, and not separated from the beginning to the end of the determination.

A piece of zinc weighing about one gram was broken off by

wrapping the larger piece in filter paper, placing it in a vise and prying with a pair of gas-pipe tongs. In this way a fragment was obtained which was wholly uncontaminated by the iron of the tools used. The outside was then removed by filing and washing with absolute ether.

The pair of crucibles 1 and 2 having been weighed, the zinc was placed in 1 and treated with an excess of nitric acid. When the metal had completely disappeared the pair was placed in a hot-air bath consisting of a large porcelain and a larger iron crucible, the space between them being filled with sand. This bath was then heated, very gently at first, afterwards more strongly, until the vapors of nitric acid and the oxides of nitrogen ceased to come off. From this bath 1 and 2 were transferred to crucible 3 (No. IV) (Fig. 3). The crucible 3 has in it a carefully fitted scorifier on which No. 2 rests. It is also supplied with a lid which is somewhat raised by means of hooks of platinum wire. To prevent sticking, the glaze is removed from the under side of the lid.

Finally, the whole arrangement, consisting of crucibles 1, 2 and 3, was placed in a muffle and heated for three hours to a temperature as high as that required for the fusion of steel. After weighing the oxide was again heated as before, but in no case was there any loss in weight after the first ignition.

IV.—*The Weighing.*

The balance used was a No. 8 long armed one made by Becker & Sons. It was supported by iron brackets fastened to one of the foundation walls of the laboratory. The following table gives the displacements of the zero point produced by one milligram:

Load.	No. Divisions on Scale.
Empty.	5.18
5 grams.	5.09
10	5.08
15	5.07
20	5.07
25	5.05
30	5.02
35	5.00
40	4.89
45	4.90
50	4.85

All weighings were made late at night, after the laboratory and the streets in its vicinity had become quiet. To determine whether the balance was sufficiently at rest for weighing, a thin glass bottle partly filled with mercury was kept in the case. In this way the slightest tremor could be detected by the agitation of the surface of the mercury. The methods of weighing by vibrations and of double weighing—that is, upon both pans—were employed throughout. Each zero point was determined by means of three series of observations, one with short, another with long, and a third with medium excursions of the pointer. The weight producing a given displacement of the zero point was not calculated from the above table of sensibility. The sensibility of the balance with the load, whatever it might be, was determined at the time of weighing, and from that the weight to be ascertained was estimated. In order to assure himself that the weighings should not be vitiated by changes in the relative lengths of the arms, the operator—having some hours beforehand closed the room, shut off the register through which the room was warmed, and lighted the lamp, which was stationed above and behind his head—would determine the position of the zero point of the empty balance. After waiting an hour, without moving from his place before the balance, he would again determine the zero point. For the same purpose the zero point was always determined just before and just after each weighing. This method is believed to be much more certain than that of placing thermometers at each end of the balance case.

The weights used belonged to a set obtained from Becker Brothers. At our request they were adjusted with the utmost care by the makers, and on comparison they showed unusually good agreement.

In order to avoid the necessity of reducing our weighings, and to make ourselves at the same time independent of the varying humidity of the atmosphere, the crucibles 1 and 2 were weighed by taring. Two crucibles of the same size, and as nearly as possible of the same weight, but slightly lighter, were selected and prepared in every respect like 1 and 2 to serve as a tare. The platinum hooks upon 1, and those upon the corresponding crucible of the tare, were brought to the same weight by filing. The weight of the tare was then brought to within less than a milligram of that of the crucibles 1 and 2 by the addition of a thin piece of porcelain obtained from a crucible of the same kind. The slight

difference between the weight of the crucibles and that of the tare could then be determined by the displacement of the zero point without the use of weights. The tares were treated with nitric acid and heated in the bath and muffle in every respect like the crucibles in which the determinations were made.

V.—*The Results.*

The method in its perfected form worked so smoothly that we were not obliged to discard a single determination. The following table contains the results of fifteen successive experiments:

	Wt. of Zinc.	Wt. of ZnO.	At. Wt. Zn. (O = 16).	At. Wt. Zn. (O = 15.96).
1	1.11616	1.38972	65.281	65.119
2	1.03423	1.28782	65.253	65.091
3	1.11628	1.38987	65.281	65.119
4	1.05760	1.31681	65.281	65.118
5	1.04801	1.30492	65.268	65.105
6	1.02957	1.28193	65.276	65.113
7	1.09181	1.35944	65.273	65.110
8	1.16413	1.44955	65.258	65.095
9	1.07814	1.34248	65.258	65.095
10	1.12754	1.40400	65.256	65.093
11	.91112	1.13446	65.272	65.109
12	1.10011	1.36981	65.264	65.101
13	1.17038	1.45726	65.273	65.111
14	1.03148	1.28436	65.263	65.100
15	1.05505	1.31365	65.277	65.114
		Mean,	65.269	65.106
		Highest,	65.281	65.119
		Lowest,	65.253	65.091
		Difference,	.028	.028

If we calculate the atomic weight from the sums of the quantities of zinc taken and oxide obtained, as recommended by Meyer and Seubert,[1] we have:

Atomic Wt. of Zn (O = 16).	Atomic Wt. of Zn (O = 15.96).
65.2693	65.1066

[1] Die Atomgewichte der Elemente, p. 13.

We give below the two series of results obtained by Marignac[1] by the analysis of the double chloride of zinc and potassium (O = 16):

1st Series.		2d Series.	
	65.26		65.28
	65.22		65.39
	65.37		65.32
	65.31		
	65.28	Mean,	65.33
Mean,	65.29	Highest,	65.39
Highest,	65.37	Lowest,	65.28
Lowest,	65.22	Difference,	0.11
Difference,	0.15		

VI.—*Objections to the Method.*

Marignac[2] has offered two objections to this method of determining the atomic weight of zinc which, if well founded, would render the results obtained by it wholly worthless; we have therefore taken great pains to investigate their validity.

These objections are:

1st. That the oxide of zinc dissociates at high temperatures.

2d. That the oxide of zinc, though heated to the temperature at which it begins to dissociate, still retains oxides of nitrogen.

To determine whether the oxide of zinc does dissociate at high temperatures, we divided about fifteen grams of the oxide, prepared from our pure metal, nearly equally between two platinum crucibles which had been tared by other crucibles of the same kind. The crucibles containing the oxide, and the tares belonging to them, were then heated for three hours in a muffle furnace to a temperature sufficient to fuse completely a ten gram piece of steel file which was placed upon a scorifier beside them. The difference between the weights of the crucibles plus the oxide and those of their tares was then determined. Afterwards the crucibles and tares were five times reheated the same length of time and as nearly as possible to the same temperature; in every case the piece of steel file placed in the muffle was fused. We give the results in tabular form.

[1] Archives des Sciences Phys. et Nat. (3) **10**, 204. [2] Ibid. **10**, 194.

SERIES I.

	Apparent Gain.	Apparent Loss.
After 1st ignition,	0.00004 gram.	...
After 2d,	0.00002	...
After 3d,	...	0.00005 gram.
After 4th,	0.00004	...
After 5th,	...	0.00004
	Total gain, 0.0001.	Total loss, 0.00009

SERIES II.

	Apparent Gain.	Apparent Loss.
After 1st ignition,	0.00006 gram.	...
After 2d,	...	0.00005 gram.
After 3d,	...	0.00001
After 4th,	0.00004	...
After 5th,	...	0.00001
	Total gain, 0.0001.	Total loss, 0.00007

It appears from these results that the oxide of zinc does not dissociate at the fusing point of steel. The interior of the platinum crucibles in which the oxide was heated did not exhibit a trace of the tarnish observed by Erdmann.[1] The apparent gain in weight of one one-hundredth of one milligram in one case, and the apparent loss of three one-hundredths of a milligram in the other, have, of course, no significance whatever.

It remained for us to find the cause of the tarnish observed by Erdmann, and of the undoubted loss of weight observed by Marignac,[2] when the oxide of zinc is heated in a platinum crucible over a flame. This we have done. In a former article[3] we have shown that the atmosphere within any platinum vessel heated by a flame receives free hydrogen, and that the phenomenon referred to is in all probability one of reduction, and not of dissociation as Marignac supposed. In that article we suggested that perhaps the platinum itself may be a cause of the dissociation of water in the flame, but more recent experiments have convinced us that this decomposition is quite independent of the presence of the platinum.

To test for the presence of the oxides of nitrogen, Marignac[4] dissolved the oxide of zinc in hydrochloric acid in the presence of

[1] Pogg. Ann. **62**, 612.
[2] This Journal **10**, 148.
[3] Archives des Sciences Phys. et Nat. (3) **10**, 195.
[4] Archives des Sciences Phys. et Nat. (3) **10**, 195.

starch and iodide of potassium. A slight blue coloration was observed. In order that this test may be relied upon, certain conditions must be fulfilled.

1st. The hydrochloric acid must be free from chlorine or any other oxidising agents.

2d. The iodide must be free from the iodate of potassium.

3d. All of the solutions must be free from absorbed oxygen.

4th. The solutions must be protected from the air.

Whether Marignac observed all of these precautions does not appear from his paper. Apparently he must have neglected some one or more of them, since we were not able with any specimen of our oxide to obtain the slightest trace of a blue coloration by this method.

To remove any chlorine contained in our hydrochloric acid we agitated the diluted acid with metallic mercury. To remove the iodate from the iodide of potassium we boiled the solution with zinc amalgam.

To remove absorbed oxygen, all of our solutions were thoroughly boiled. The order in which the materials were brought together is as follows: The boiling solution of iodide was poured into the boiling starch paste in an Erlenmeyer flask. To this mixture was added first the zinc oxide and then the boiling hydrochloric acid. The steam rising from the liquid sufficed to protect it from the air.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

THE REMOVAL OF IODATE FROM THE IODIDE OF POTASSIUM BY MEANS OF ZINC AMALGAM.

BY H. N. MORSE AND W. M. BURTON.

The frequent occurrence of the iodate of potassium in the commercial iodide, and the difficulty of removing it, are two of the most serious obstacles in the way of the free use of the iodometric method, either for quantitative work, or for the detection of oxidising agents. The fact that so many methods have been

proposed for the preparation of iodide free from the iodate, and for the removal of the latter from the former, indicates that a simple and effective method for the preparation of the pure iodide of potassium is much needed, but not readily found.

In the course of our work upon the atomic weight of zinc it became necessary for us to prepare some iodide of potassium free from iodate, in order to test for the presence of the oxides of nitrogen, which Marignac[1] supposes to remain in the oxide of zinc prepared from the nitrate, even up to the dissociating temperature of the oxide. The method which we employed for the purpose consists in boiling the solution of the iodide with zinc amalgam. By this means the iodate is completely reduced with formation of zinc hydroxide, and the filtered solution is found to be free from both mercury and zinc. It is recommended to make the amalgam quite rich in zinc, and to have the filter paper, through which the hot solution of iodide is to be filtered, saturated with boiling water. The efficacy of the method was tested upon solutions of pure iodate of potassium. In one case one gram of the iodate dissolved in 50 cubic centimeters of water was completely reduced within forty-five minutes; in another, two grams dissolved in the same amount of water were reduced within one hour and a quarter. The bromate and chlorate of potassium are also reduced by zinc amalgam, but much more slowly than the iodate. Of the two, the chlorate reduces less rapidly than the bromate.

The zinc amalgam used in the reduction is best prepared by agitating zinc dust with mercury in the presence of tartaric acid and washing with water.

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A METHOD FOR THE ANALYSIS OF BUTTER, OLEOMARGARINE, ETC.

BY H. N. MORSE AND W. M. BURTON.

The method which we here describe has been in use in this laboratory during the past year. Its advantages are: 1st. That it

[1] Archives des Sciences Phys. et Nat. (3) **10**, 195.

is volumetric throughout; 2d. That it obviates the necessity of weighing the specimen of fat; 3d. That it readily discriminates between genuine butter and any mixture of cocoanut oil and other fats or oils. That is, it succeeds at that point where the methods of Hehner and of Koettstorfer may fail.

It depends upon the fact that the relative quantities of alkali required to neutralise the soluble and insoluble acids are for any one fat or oil quite constant, but for different fats or oils quite variable.

The following statement contains the relative percentages of alkali required to neutralise the soluble and insoluble acids of butter, cocoanut oil, cottonseed oil, oleomargarine, lard, and beef tallow:

	Per cent. KOH required for insoluble acids.	Per cent. KOH required for soluble acids.
1. Butter	86.57	13.17
2. Cocoanut oil (unwashed),	91.95	8.17
3. Cocoanut oil (washed with hot water)	92.43	7.42
4. Cocoanut oil (washed with dilute Na_2CO_3) . .	92.33	7.45
5. Cottonseed oil	92.05	7.76
6. Oleomargarine	95.40	4.57
7. Lard	95.96	3.82
8. Beef tallow	96.72	3.40

There is, between the amounts of alkali required to neutralise the soluble acids of butter and of unwashed cocoanut oil, a clear difference of 5 per cent.

Evidently it would not be possible to make any mixture of the other substances than butter in this list which would not show even a greater divergence from butter in respect to the soluble acids. The only way in which the proportion of soluble acids can be increased beyond 8.17 per cent. is by the addition of butter itself.

It was found by Moore[1] that a mixture of butter 50 per cent., oleomargarine 27.5 per cent., and cocoanut oil 22.5 per cent., could not be distinguished from butter either by the method of Hehner or by that of Koettstorfer. Such a mixture gave us:

Per cent. KOH required for insoluble acids.	Per cent. KOH required for soluble acids.
90.17	9.70

[1] This Journal 6, 418.

There is still a difference in respect to soluble acids of 3.47 per cent. between such a mixture and butter; and it would not be practicable to so far increase the proportion of butter that there would not still be a perceptible difference in this respect between genuine butter and the mixture. The figures thus far given are mean quantities; we give in the following table the individual results from which they were calculated. The first column contains the number of milligrams of potassium hydroxide required to saponify one gram of fat; the second and third columns, the number of milligrams required to neutralise the insoluble and soluble acids contained in one gram of the fat; while the fourth and fifth give the percentages corresponding to the quantities in two and three.

A. *Butter.*

	I. Mgs. KOH for 1 gram fat.	II. Mgs. KOH for insoluble acids.	III. Mgs. KOH for soluble acids.	IV. Per cent. KOH for insoluble acids.	V. Per cent. KOH for soluble acids.
1.	230.39	199.57	30.21	86.62	13.11
2.	231.14	199.83	30.94	86.45	13.38
3.	230.66	200.11	30.07	86.75	13.04
4.	230.71	199.67	30.54	86.53	13.23
5.	230.94	199.85	30.29	86.53	13.11
				Mean, 86.57	13.17

B. *Cocoanut Oil* (unwashed).

1.	266.88	245.50	21.91	91.98	8.20
2.	266.96	244.87	22.01	91.72	8.24
3.	266.58	245.68	21.53	92.15	8.07
				Mean, 91.95	8.17

Cocoanut Oil (washed with hot water).

4.	262.44	243.17	19.11	92.65	7.28
5.	263.33	242.84	19.91	92.21	7.56
				Mean, 92.43	7.42

Cocoanut Oil (washed with dilute Na_2CO_3).

1.	263.73	243.27	19.91	92.24	7.54
2.	263.42	243.39	19.31	92.39	7.33
3.	263.97	243.81	19.57	92.36	7.41
4.	264.22	243.96	19.50	92.33	7.38
5.	263.82	243.61	20.03	92.33	7.59
				Mean, 92.33	7.45

C. *Cottonseed Oil.*

1.	200.23	184.31	15.57	92.04	7.77
2.	200.54	184.04	15.71	91.77	7.83
3.	199.74	184.26	15.06	92.25	7.54
4.	199.81	183.72	15.36	91.95	7.68
5.	199.65	184.18	15.92	92.25	7.97
				Mean, 92.05	7.76

D. *Oleomargarine.*

1.	202.70	193.02	9.31	95.22	4.59
2.	202.61	193.46	9.01	95.48	4.44
3.	202.40	193.21	9.71	95.45	4.79
4.	202.62	193.65	9.21	95.57	4.54
5.	202.83	193.27	9.12	95.28	4.49
				Mean, 95.40	4.57

E. *Lard.*

1.	199.77	191.78	7.31	96.00	3.65
2.	198.93	191.11	7.91	96.06	3.98
3.	199.54	191.29	7.71	95.86	3.94
4.	199.75	191.62	7.87	95.93	3.94
5.	199.40	191.34	7.17	95.97	3.59
				Mean, 95.96	3.82

F. *Beef Tallow.*

1.	200.44	193.43	6.76	96.50	3.37
2.	199.70	193.20	6.92	96.74	3.46
3.	200.17	193.81	6.47	96.82	3.23
4.	199.60	193.13	6.91	96.76	3.46
5.	199.84	193.42	7.01	96.78	3.50
				Mean, 96.72	3.40

G.	*Mixture:* Oleomargarine 27.5; Cocoanut Oil 22.5; Butter 50 per cent.				
1.	231.	208.77	22.65	90.37	9.81
2.	230.82	208.13	22.21	90.16	9.62
3.	231.15	208.11	22.76	90.03	9.84
4.	231.36	208.51	22.16	90.12	9.57
				Mean, 90.17	9.70
			Percentages for pure butter,	86.57	13.17
				Difference, 3.60	3.47

The Reagents.

1. A solution of hydrochloric acid of such strength that one cubic centimeter of it is equivalent to 20 milligrams of potassium hydroxide.

2. A solution of hydrochloric acid one tenth as strong as the first.

3. A solution of potassium hydroxide in 95 per cent. alcohol approximately equivalent to the first acid.

4. A solution of potassium hydroxide in 95 per cent. alcohol one tenth as strong as the preceding.

The Mode of Procedure.

The dry and filtered fat is well stirred during solidification, to prevent the separation of the lower from the higher melting constituents.

Any convenient quantity of the material, between one and two grams, is placed in an Erlenmeyer flask having a capacity of 250 cubic centimeters, and treated with that amount of alkali which is found to be equivalent to 40 cubic centimeters of the acid No. 1. The flask is then placed upon the water-bath and heated to the boiling point of alcohol for 20 minutes.

The excess of alkali is determined by acid No. 1, with the use of phenolphthalein as the indicator. Thus the number of milligrams of KOH required for the neutralisation of all of the acids in the fat is found. The flask is then returned to the water-bath and heated until all of the alcohol has been expelled. During the evaporation of the alcohol, the soap, which in the first place was neutral, becomes alkaline, owing doubtless to the evaporation of

a small amount of volatile acids in the form of esters; but the loss from this cause is very slight.[1] When the odor of alcohol is no longer perceptible the soap is treated with that quantity of acid No. 1 which is necessary to exactly liberate all of the acids contained in it. This quantity is, of course, the difference between 40 and the number of cubic centimeters required to neutralise the excess of the alkali used in saponification. The flask is again returned to the water-bath and heated until the liquid becomes clear. But, in order to prevent loss of volatile acids, it is now supplied with a stopper carrying a glass tube about 5 millimeters in diameter and 400 millimeters in length. The upper end of the tube is bent downwards, and to it is attached a small U-tube containing a few cubic centimeters of water. The contents of the flask are filtered through double thick paper which has been wet with hot water and then washed with boiling water until the volume of the filtrate equals a liter; care being taken to wash thoroughly the flask itself. The contents of the condensing arrangement are washed into the filtrate. The funnel containing the washed insoluble acids is placed in the flask in which the saponification, etc., were effected, the paper pierced, and the contents washed through with hot 50 per cent. alcohol.

We thus have the soluble and insoluble acids separated, and it only remains to determine the amount of alkali required to neutralise each. The soluble acids can be directly determined by the weaker solution of the alkali; but to determine the insoluble acids it is better to add the quantity of alkali which was required for the total saponification, and, after warming upon the water-bath, to titrate back with the weaker acid. It will be observed that a determination of the insoluble acids alone by this method suffices to distinguish butter from other fats and mixtures, and that if these only are to be determined it is not necessary to use the condensing arrangement. Moreover, it is not necessary to know the exact strength of the solutions employed, since a knowledge of the relation of the acids to each other and to the alkalies is all that is needed to enable us to determine, in the fat, the relation of the soluble to the insoluble acids. Hence it is practicable to dispense

[1] This loss may be made good by bringing the solution to a neutral condition by means of very dilute acetic acid. The quantity of acetic acid thus introduced is, of course, equivalent to the acid which has been lost during the evaporation of the alcohol. We are under the impression that there is no such loss of volatile acids during saponification, owing to the presence of a considerable excess of alkali.

with the use of the balance altogether. It is frequently recommended to make blank determinations, in order to control the error introduced by the action of the alkali upon the glass of the flasks. But a little reflection will convince one that this practice may itself be the cause of considerable error, inasmuch as the extent to which the glass is affected by the alkali depends upon its quality and upon the treatment to which it has previously been subjected. In order that the results of the blank may be applied to the correction of those of the determinations, it is necessary that the glass employed in the two cases should be the same in respect to composition and previous use in the laboratory. It is better, according to our experience, to discard the use of blanks and to boil out with strong alkali all flasks employed in such work. The subsequent action of dilute alkali upon glass which has been treated this way is very slight. The water and alcohol employed in making the standard solutions should of course be thoroughly boiled, and afterwards protected from the carbon dioxide of the air by keeping them in bottles or flasks which are supplied with stoppers carrying tubes filled with soda-lime. The use of blanks is then not necessary on account of any *carbonic* acid contained in the solution.

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CATALPIN: A BITTER PRINCIPLE.

BY EDO CLAASSEN.

Catalpin is contained in the bark and fruit of Catalpa bignonioides, Wal., a tree which, though not indigenous, is largely cultivated in the northern United States on account of its showy flower and handsome, bean-like fruit. To obtain the principle, the fruit, deprived of its seeds, which contain no catalpin, glucose, and but about 24 per cent. of thick yellow oil, or the bark, which is richer in catalpin than the fruit, was extracted with alcohol, the alcohol evaporated, the residue dissolved in water, lead acetate added, the filtrate mixed with baric carbonate, evaporated to a thin syrup, extracted with a mixture of ether and alcohol (3 : 1),

the solution evaporated, the residue dissolved in water, and the solution filtered and concentrated. As the filtrate yielded no crystals, even after long standing, it was shaken with a comparatively large quantity of freshly ignited animal charcoal, which, on standing for 24 hours, extracted the bitter principle. The charcoal was filtered and thoroughly washed with water, then dried and extracted with boiling alcohol, the alcohol evaporated, the residue dissolved in water, the solution filtered, concentrated, and allowed to crystallise. Colorless crystals were obtained by recrystallisation. As the mother liquors contained a large proportion of the catalpin, they were concentrated, treated with lead subacetate, shaken with ether to remove impurities, and after dilution of the residue with water, the latter decomposed by hydric sulphide. The filtrate was, after the addition of baric carbonate, evaporated to a thin syrup, extracted with ether and alcohol (3 : 1), the ether and alcohol driven off, the residue dissolved in water, concentrated, and allowed to crystallise. The difficulty of isolating the bitter principle arises, probably, not so much from its solubility as from its slight tendency to crystallise, in consequence of which small quantities of other substances prevent its crystallisation.

Catalpin forms radial aggregates of white acicular or silky, slender, and often curved crystals. On heating, it first melts to a colorless liquid, then evolves a vapor with a peculiar odor, and is entirely consumed. It is quite soluble in cold and very soluble in hot water, easily soluble in alcohol, and only with difficulty in ether. It is insoluble in benzene, nearly insoluble in chloroform, and soluble in amyl alcohol, especially if hot. Chloroform precipitates it from its solution in amyl alcohol in very small radial aggregations, and from its solution in ethyl alcohol in radial aggregations of long tufted silky needles. It is a glucoside, and does not reduce alkaline copper solution unless it is first boiled with dilute sulphuric acid. In a solution of catalpin, tannin produces no precipitate nor turbidity, even after addition of dilute sulphuric acid; but if this mixture is boiled, it becomes turbid on cooling. It does not act upon ammoniacal silver solution, ferric chloride, lead acetate, phosphomolybdic acid, phosphomolybdic acid and ammonia, potassium mercuric iodide, or solution of iodine in potassic iodide. It is precipitated by lead subacetate. It reduces gold chloride after standing with it several days. Concentrated

hydrochloric acid and concentrated potassic hydrate solution dissolve it without change of color. The solution in cold concentrated nitric acid, colorless at first, soon becomes yellow, and on heating, reddish yellow. Concentrated sulphuric acid turns it dark at once, and dissolves it with a violet color. An addition of a little nitric acid changes this first to light brownish red and then reddish brown.

THE ELECTROLYTIC METHOD AS APPLIED TO IRON.

By Edgar F. Smith.

In estimating this metal by electrolysis I have employed solutions containing an excess of sodium citrate with a little free citric acid. In the first experiments I made use of ferric ammonium sulphate solutions of unknown strength. The volume of the liquid electrolysed varied from 76–150 cc. The electric current liberated 6 cc. of oxy-hydrogen gas per minute. The time required for the complete precipitation of the metal was from 4 to 8 hours; in most cases it was finished in four hours. Some of the results are as follows:

(1) Deposit of iron + platinum dish = 68.6548 grams.
(2) Deposit of iron + platinum dish = 68.6550 grams.
(3) Deposit of iron + platinum dish = 68.6548 grams.
(4) Deposit of iron + platinum dish = 68.6554 grams.

The residual liquid in these experiments was found to contain no iron.

I next dissolved pure ferric ammonium sulphate in a definite volume of water: in 10 cc. of this solution I obtained, by the usual method of analysis, .0147 gram of metallic iron. Working under conditions similar to those mentioned above, I found:

(1) .0145 gram Fe. (2) .0145 gram Fe. (3) .0143 gram Fe. (4) .0150 gram Fe.

The deposit of (3) was not uniform; particles became detached in the operation of washing and passed into the filtrate, giving evidences of the presence of iron upon subsequent testing. With

30 cc. of the same solution the iron deposit weighed .0448 gram instead of the theoretical .0441 gram.

Continuing the work with iron solutions in 10 cc. of which .0300 gram Fe was present; using a sodium citrate solution, obtained by dissolving 28 grams of air-dried salt in 250 cc. water, I made the determinations as follows:

I. 5 cc. ferric ammonium sulphate (equivalent to .0150 gram Fe) and 10 cc. sodium citrate solution, with a few drops of citric acid, were diluted to 150 cc. and electrolysed with a current generating 12 cc. oxy-hydrogen gas per minute. Found .0149 gram Fe instead of .0150 gram. The current was allowed to act for six hours.

II. Same as I; gave .0152 gram Fe.

III. Same as I and II, except that the entire volume of solution did not exceed 40 cc. The electrolysis was performed in a platinum crucible. Obtained .0151 gram Fe.

IV. 10 cc. iron solution (equivalent to .0300 gram Fe), 20 cc. sodium citrate, and some free citric acid, subjected to the action of a current producing 15 cc. oxy-hydrogen gas per minute, gave .0303 gram Fe. The volume of liquid was 100 cc. Time for precipitation four and a half hours

V. 5 cc. iron solution, treated as in I, gave .0149 gram Fe.

VI. 10 cc. iron solution, under the same conditions as IV, afforded .0304 gram Fe.

VII. 5 cc. iron solution gave .0151 gram Fe.

With a third solution of iron, containing .0210 gram Fe in 10 cc. of the same, I obtained:

(1) .0104 gram in 5 cc. (2) .0104 gram Fe in 5 cc. (3) .0206 gram Fe in 10 cc.

The total volume of liquid in each case amounted to 150 cc. The volume of sodium citrate solution (same strength as above) was increased to 30 cc. in these three determinations. The current had the same strength as before.

The iron deposit in all the experiments was compact, regular, and steel-like in appearance. It was washed with water, alcohol and ether, then dried and weighed. Several deposits were exposed for weeks to the air of the balance room without undergoing any alteration. In experiment VII considerable aluminium was present as sulphate. To two others I added a solution of titanium; the precipitated iron was found to be entirely free of this metal. Solu-

tions of titanium alone, when treated just as the iron solutions were, gave no deposit. The above experiments were conducted in the cold. An account of the experiments made with a view of separating iron and titanium by electrolysis will be given later.

CHEMICAL LABORATORY OF WITTENBERG COLLEGE, *May* 3, 1888.

NOTES.

On the Influence of Light upon the Explosion of Nitrogen Iodide.

The statement of L. Gattermann in his recent paper (*Berichte d. deutsch. chem. Gesellsch.* **21**, 751; following up V. Meyer's paper in same vol., 26) on nitrogen chloride, that its explosive decomposition may be brought about, or its susceptibility to explosion much increased, by exposure to bright light, has recalled to my mind the fact, which did not specially impress me at the time, that I myself undoubtedly observed the same relation several years ago in the case of nitrogen iodide.

In a paper on the preparation and composition of the latter substance, published in the first number of this Journal (April, 1879), it was noted that on two occasions the product obtained with the composition NI_3 or N_2I_6 "exploded in some quantity *under water* with much violence and complete shattering of the vessel."

I remember distinctly that in one of these cases I had just carried to a window, through which the sun was shining, the beaker full of water at the bottom of which was the black sediment of iodide, and was gently stirring the liquid with a glass rod, holding the beaker up so as to look at it from below, when the rod touched the lower part of the side or the bottom of the vessel, and the explosion occurred.

In the other case the iodide was being washed with ice-cold water of ammonia, the vessel standing on a table exposed at the time to the direct rays of the sun. I do not remember with certainty what seemed to precipitate the explosion on this occasion, but I believe it was the pouring some fresh liquid, from the height of a few inches, on the black sediment of iodide which had just been partially drained by decantation.

Under ordinary circumstances nitrogen iodide, while *wet*, exhibits no extraordinary sensitiveness, and may be safely worked with, only becoming highly dangerous on drying, so that I have little doubt that bright sunlight was influential in bringing about these two explosions. J. W. MALLET.

UNIVERSITY OF VIRGINIA, *May* 8, 1888.